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LXXVII. *On the Steady Motion of Viscous, Incompressible Fluids; with particular reference to a Variation Principle.*
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1. *Introduction.*

A DISCUSSION of the general equations for steady motion of a viscous, incompressible fluid from the point of view of a minimum or variation principle has, as far as the writer is aware, never been given. Helmholtz, in a classical paper † “On the Theory of a Stationary Flow in Viscous Liquids,” has shown that if the quadratic terms in velocity be neglected, if the velocities at the boundary of a singly-connected region be kept constant, and if the external forces have a single-valued potential, then the motion is such that the variation of the energy dissipation in the region under consideration is zero. We shall refer to this work in more detail later. Korteweg subsequently showed ‡ that under the above conditions the steady motion which is set up is unique and stable, *i. e.*, the dissipation for this motion is an absolute minimum. Rayleigh §, still later, showed that the dissipation is an absolute minimum whenever $\nabla^2 q = \nabla H$,

* Communicated by Prof. H. Bateman, Ph.D.

† H. Helmholtz, ‘Collected Works,’ p. 223.

‡ D. J. Korteweg, *Phil. Mag.* xvi. p. 112 (1883).

§ Lord Rayleigh, *Phil. Mag.* xxvi. p. 776 (1913); *Coll. Works*, vi. p. 167.

where \mathbf{q} is the vector velocity of the fluid, and H is a single-valued function subject to the condition $\nabla^2 H = 0$. In this case there is no restriction upon the magnitude of the velocity. As far as the author is aware, this represents practically the entire extent of the work to date on the application of a minimum principle to the steady motion of a viscous fluid*.

In the present work we discuss the following problem: given an incompressible, viscous fluid with fixed (if any) boundaries, to find a function L , such that if we set

$$\delta \int_V L d\tau = 0,$$

where δ is the symbol representing variation, then the Eulerian equations corresponding to this equation are exactly the Navier-Stokes equations for the motion of the fluid. The integral is (for three-dimensional cases) a volume integral, and $d\tau$ represents the volume element. We impose, of course, the customary condition that the variation of the velocity is taken to be zero at the boundaries of the region considered. We shall for simplicity refer to such a function L as a Lagrangian function, in spite of the fact that the term is not strictly accurate.

In the second section we set up a Lagrangian function by generalizing the considerations of Helmholtz relative to slow motion, and from the resulting Eulerian equations are led to a proof of the following theorem:—

“If L be restricted to be a function of the velocity components and their first-order space derivatives only, then it is impossible to find any such L which will give the general equations for steady flow of an incompressible fluid, through the application of the variation principle described above.”

The conditions which must be imposed on the motion in order that it may correspond to a variation principle, involving a Lagrangian function of this type, are discussed, and it is shown that all of the cases of steady motion which have thus far been discovered satisfy these conditions.

In the third section the Lagrangian functions are found for the cases of plane laminar motion, and Poiseuille flow through a circular tube.

* J. Brill (Proc. Camb. Phil. Soc. viii. p. 313, 1895) has discussed a minimum principle for a case similar to that of Rayleigh. H. Bateman, in some unpublished work, has recently discussed variation principles for the general viscous equations of motion, which contain arbitrary auxiliary functions and do not in general reduce to minimum principles.

The fourth section does not strictly form a part of the general variation problem, but the results obtained in it are used in the subsequent section, and have also a certain amount of interest on their own account. Formulæ are given for the transformation of certain expressions from vector to curvilinear coordinate form, and a vector expression independent of coordinate systems is deduced for the dissipation function.

In the fifth section the variation problem for two-dimensional flow in logarithmic spirals is discussed, and the corresponding Lagrangian function is exhibited.

The analysis throughout takes no account of body forces, since, if such forces do occur and have a single-valued potential, they may be taken account of in the pressure terms, without in any way altering the form of the equations. The vector method is used whenever it appears convenient, and in such cases the notation is that of Gibbs, involving the operator ∇ . Symbols denoting vector quantities are printed in bold-faced type, while the absolute value or magnitude of these quantities is denoted by the same symbols printed in normal type. In order to follow the customary use of symbols, it has been deemed advisable to change notation in the middle of the paper. In the second and third sections, involving primarily Cartesian coordinate systems, the velocity components are denoted by u, v, w . In the last two sections these symbols are used to represent curvilinear coordinates, and the velocity components are denoted by q with appropriate subscripts. The conventional subscript notation for differentiation is frequently used, the subscript 1 implying differentiation with respect to x , 2 differentiation with respect to y , etc., unless otherwise specified.

2. *On the Existence of a Lagrangian Function in General.*

We have, for steady motion of a viscous, incompressible fluid, the Navier-Stokes equations of motion, which may be combined into the single vector equation

$$\rho(\mathbf{q} \cdot \nabla)\mathbf{q} + \nabla p = \mu \nabla^2 \mathbf{q}, \quad . \quad . \quad . \quad (1)$$

where \mathbf{q} represents the vector velocity of the fluid, p the pressure, ρ the density, and μ the coefficient of viscosity (the last two being assumed constant throughout this paper). In addition we have the equation of continuity,

$$\nabla \cdot \mathbf{q} = 0. \quad . \quad . \quad . \quad (2)$$

Following Helmholtz, we define P as the rate at which

work is done by the external forces (in our case pressure and viscosity forces) upon the fluid in the particular volume region we happen to discuss, and Q as the rate of dissipation of energy inside the region. We introduce a new quantity R , which we define to be the rate at which kinetic energy is carried out of the region across the boundary. We wish later to discuss the values of the above quantities per unit volume, and hence define the "density functions" \mathbf{P} , \mathbf{R} , Φ as follows:—

$$\left. \begin{aligned} \mathbf{P} &= \int_V \mathbf{P} \, d\tau, \\ \mathbf{R} &= \int_V \mathbf{R} \, d\tau, \\ \mathbf{Q} &= \int_V \Phi \, d\tau, \end{aligned} \right\} \dots \dots \dots (3)$$

where V is the volume region considered. Φ is usually called the dissipation function, and is given by *

$$\Phi = \mu \{ 2u_1^2 + 2v_2^2 + 2w_3^2 + (w_2 + v_3)^2 + (u_3 + w_1)^2 + (v_1 + u_2)^2 \}, \dots \dots (4)$$

where x, y, z are Cartesian coordinates, u, v, w are the corresponding velocity components, and the subscripts denote differentiation. This is the general expression for Φ for any viscous fluid; the condition of incompressibility has not been introduced in its derivation.

In Helmholtz case of slow motion, squares of velocity are neglected, and hence $R=0$. Therefore the equation of conservation of energy is $\mathbf{P}-\mathbf{Q}=0$. Helmholtz showed that in this case, even if there are immersed bodies in the fluid so that the boundary conditions are less specified than ours, if one writes

$$\delta(\mathbf{P} - \tfrac{1}{2}\mathbf{Q}) = 0,$$

one is led to the equation of motion with quadratic terms omitted,

$$\nabla p = \mu \nabla^2 \mathbf{q}.$$

In our more general case the equation of energy becomes

$$\mathbf{P} - \mathbf{Q} - \mathbf{R} = 0, \dots \dots \dots (5)$$

and one is led to try as a variation principle

$$\delta(\mathbf{P} - \tfrac{1}{2}\mathbf{Q} - \gamma \mathbf{R}) = 0, \dots \dots \dots (6)$$

* H. Lamb, 'Hydrodynamics,' 5th ed. p. 549.

where γ is a numerical coefficient to be determined empirically. We remark first that P may be written as a surface integral extended over the boundary of the region. Hence, after performing the variation, we get from this term another surface integral with components of $\delta \mathbf{q}$ as multiplying factors. But in Helmholtz's case, if we rule out immersed bodies, and in our case, the variation of velocity is assumed to be zero at the boundary. Hence the term P contributes nothing to the Eulerian equations, and may be entirely omitted in the evaluation of (6). We remark next that the variation is to be taken subject to the restriction given by the continuity equation (2). We introduce this restriction in the customary manner, namely through the use of a Lagrangian undetermined multiplier. In view of these remarks and using equations (3), we may write equation (6) in the following form :—

$$\delta \int_V \{ \frac{1}{2} \Phi + \gamma \mathbf{R} - \lambda \nabla \cdot \mathbf{q} \} d\tau = \delta \int_V L d\tau = 0, \quad (7)$$

where λ is the Lagrangian undetermined multiplier.

In evaluating this expression it is convenient to use Cartesian coordinates. The expression for Φ is then given by equation (4), and \mathbf{R} remains to be evaluated. From the definition of \mathbf{R} we have, where S is the bounding surface of the region V , ds is the surface element, and \mathbf{n} is a unit vector in the direction of the outwardly-drawn normal at ds ,

$$\mathbf{R} = \frac{\rho}{2} \int_S q^2 \mathbf{n} \cdot \mathbf{q} ds = \frac{\rho}{2} \int_S \mathbf{n} \cdot (q^2 \mathbf{q}) ds,$$

and applying the divergence theorem,

$$\mathbf{R} = \frac{\rho}{2} \int_V \nabla \cdot (q^2 \mathbf{q}) d\tau = \frac{\rho}{2} \int_V (q^2 \nabla \cdot \mathbf{q} + \mathbf{q} \cdot \nabla q^2) d\tau,$$

and hence, because of the continuity equation,

$$\mathbf{R} = \frac{\rho}{2} \int_V \mathbf{q} \cdot \nabla q^2 d\tau,$$

or

$$\mathbf{R} = \frac{\rho}{2} \mathbf{q} \cdot \nabla q^2. \quad \dots \dots \dots (8)$$

In Cartesian coordinates this gives

$$\mathbf{R} = \rho \{ u^2 u_1 + uvv_1 + uww_1 + uvu_2 + v^2 v_2 + vww_2 \\ + uvu_3 + vwr_3 + w^2 w_3 \}.$$

Hence the function L , defined in (7), becomes

$$L = \mu \{ u_1^2 + v_2^2 + w_3^2 + \frac{1}{2}(w_2 + v_3)^2 + \frac{1}{2}(u_3 + w_1)^2 + \frac{1}{2}(v_1 + u_2)^2 \} \\ + \gamma \rho \{ u^2 u_1 + uvv_1 + uww_1 + uvu_2 + v^2 v_3 + vww_2 \\ + uww_3 + vvv_3 + w^2 w_3 \} \\ - \lambda \{ u_1 + v_2 + w_3 \}.$$

The Eulerian equations corresponding to equation (7) are

$$\frac{\partial}{\partial x} \left(\frac{\partial L}{\partial u_1} \right) + \frac{\partial}{\partial y} \left(\frac{\partial L}{\partial u_2} \right) + \frac{\partial}{\partial z} \left(\frac{\partial L}{\partial u_3} \right) - \frac{\partial L}{\partial u} = 0,$$

with two analogous equations for v and w . Substituting our expression for L into this equation, we have

$$\mu \{ 2u_{11} + u_{22} + v_{12} + u_{33} + w_{13} \} \\ + \gamma \rho \{ uv_2 + uw_3 - vv_1 - ww_1 \} - \lambda_1 = 0$$

(where double subscripts signify the appropriate second derivatives), or

$$\mu \left\{ \nabla^2 u + \frac{\partial}{\partial x} (\nabla \cdot \mathbf{q}) \right\} + \gamma \rho \left\{ \mu \nabla \cdot \mathbf{q} - \frac{1}{2} \frac{\partial q^2}{\partial x} \right\} - \frac{\partial \lambda}{\partial x} = 0,$$

and introducing the continuity equation :

$$\mu \nabla^2 u - \gamma \rho \frac{1}{2} \frac{\partial q^2}{\partial x} - \frac{\partial \lambda}{\partial x} = 0;$$

and, finally, combining with the two analogous equations deduced from the other two Eulerian equations, we have the vector equation :

$$\gamma \rho \frac{1}{2} \nabla q^2 + \nabla \lambda = \mu \nabla^2 \mathbf{q}. \quad . \quad . \quad . \quad (9)$$

If, now, we change notation, writing p for λ , and if we take the numerical coefficient γ to be 1, then equation (9) is just the Navier-Stokes equation (1), except that $(\mathbf{q} \cdot \nabla) \mathbf{q}$ is replaced by $\frac{1}{2} \nabla q^2$.

Hence, whenever conditions are imposed on the motion, of such a nature that the terms $(\mathbf{q} \cdot \nabla) \mathbf{q}$ are replaced by $\frac{1}{2} \nabla q^2$, then in such cases the equations of motion may be deduced from the variation principle given in equation (6). Since we have the general vector relation

$$(\mathbf{q} \cdot \nabla) \mathbf{q} = \frac{1}{2} \nabla q^2 - \mathbf{q} \times \text{curl } \mathbf{q},$$

we see that the condition just mentioned is satisfied in the more or less trivial case in which $\mathbf{q} \times \text{curl } \mathbf{q} = 0$, which implies either that the vorticity is everywhere zero, or that it is everywhere parallel to the velocity. We shall later

discuss several other more interesting cases in which the condition is satisfied. At present we wish to continue with our more general considerations.

If we express $(\mathbf{q} \cdot \nabla)\mathbf{q}$ in Cartesian form, we have

$$[(\mathbf{q} \cdot \nabla)\mathbf{q}]_x = uu_1 + vu_2 + wu_3$$

(similarly for y and z components), and hence it appears that the terms in the equations of motion which the variation principle does not give are

$$vu_2, wu_3, \text{ and } wv_3, uv_1, uw_1, vw_2. \quad . \quad . \quad (10)$$

We are therefore led to a consideration of the possibility of obtaining terms of this form from any Lagrangian function involving the velocity components and their first-order space derivatives. It will suffice to discuss only one of the terms mentioned, together with the single Eulerian equation corresponding to it. Then by cyclic substitution the analysis can be extended to all of the other terms. We state the problem as follows:—

“ Given the Eulerian equation

$$\text{E.F.} = \frac{\partial}{\partial x} \left(\frac{\partial L}{\partial u_1} \right) + \frac{\partial}{\partial y} \left(\frac{\partial L}{\partial u_2} \right) + \frac{\partial}{\partial z} \left(\frac{\partial L}{\partial u_3} \right) - \frac{\partial L}{\partial u} = 0,$$

where we shall call the left side of this equation the ‘Eulerian Function’ and denote it for convenience by E.F. To find a function

$$L = L(u, v, w, u_1, u_2, u_3, v_1, v_2, v_3, w_1, w_2, w_3), \quad . \quad (11)$$

such that if we introduce this function into the Eulerian equation, we get

$$\text{E.F.} = vu_2 + t = 0, \quad . \quad . \quad . \quad (12)$$

where t is a sum of any of the other terms in the x -component Navier-Stokes equation (1).”

It is obvious at once, since vu_2 cannot be obtained from any expression of the form $\frac{\partial f}{\partial x}$ or $\frac{\partial g}{\partial z}$, where f and g are any functions of the velocities and their space derivatives, that for the present purpose the Eulerian Function may be simplified and written :

$$\text{E.F.} = \frac{\partial}{\partial y} \left(\frac{\partial L}{\partial u_2} \right) - \frac{\partial L}{\partial u}.$$

Consider, first,

$$L = u^\alpha v^\beta w^\gamma u_1^{\alpha_1} u_2^{\alpha_2} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3}, \quad . \quad (13)$$

where the exponents are any real numbers. The Eulerian Function corresponding to this L is

$$\begin{aligned} \text{E.F.} = & v^{\beta} u_2^{\alpha_2} \{ \alpha_2 \alpha u^{\alpha-1} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} \\ & - \alpha u^{\alpha-1} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} \} \\ & + v^{\beta} u_2^{\alpha_2-1} \{ \alpha_2 \gamma u^{\alpha} w^{\gamma-1} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2+1} w_3^{\gamma_3} \\ & + \alpha_2 \alpha_1 u^{\alpha} w^{\gamma} u_1^{\alpha_1-1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} u_{12} \\ & + \alpha_2 \alpha_3 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3-1} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} u_{23} \\ & + \alpha_2 \beta_1 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1-1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} v_{12} \\ & + \alpha_2 \beta_2 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2-1} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} v_{22} \\ & + \alpha_2 \beta_3 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3-1} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} v_{23} \\ & + \alpha_2 \gamma_1 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1-1} w_2^{\gamma_2} w_3^{\gamma_3} w_{12} \\ & + \alpha_2 \gamma_2 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2-1} w_3^{\gamma_3} w_{22} \\ & + \alpha_2 \gamma_3 u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3-1} w_{23} \} \\ & + v^{\beta} u_2^{\alpha_2-2} \{ \alpha_2 (\alpha_2 - 1) u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} u_{22} \} \\ & + v^{\beta-1} u_2^{\alpha_2-1} \{ \alpha_2 \beta u^{\alpha} w^{\gamma} u_1^{\alpha_1} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2+1} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3} \}. \end{aligned} \quad \dots (14)$$

From this equation it appears that there are four possible combinations of values of β and α_2 which could give vu_2 :—

(1) $\beta = \alpha_2 = 1$. In this case the terms in the bracket multiplying vu_2 cancel, and the entire term involving vu_2 vanishes.

(2) $\beta = 1, \alpha_2 = 3$. Here there is a factor u_{22} multiplying vu_2 which cannot be made to disappear. Hence this combination does not give an expression of the form (12).

(3) $\beta = \alpha_2 = 2$. In this case the additional conditions that we get a term of the form vu_2 are

$$\alpha = \gamma = \alpha_1 = \alpha_3 = \beta_1 = \beta_3 = \gamma_1 = \gamma_2 = \gamma_3 = 0, \quad \beta_2 = -1.$$

Hence

$$L = \frac{v^2 u_2^2}{v_2},$$

and the Eulerian Function becomes

$$\text{E.F.} = 4vu_2 + 2 \frac{v^2}{v_2} u_{22} - 2 \frac{v^2 u_2}{v_2^2} v_{22}.$$

The last two terms of this expression do not appear in the

equations of motion. Hence we must find a second function L' to be subtracted from L , where L' gives these extraneous terms. But both of these terms have second derivatives as multiplying factors, and from (14) we see that any such term involving second derivatives occurs in the Eulerian Function in a single, unique manner; *i. e.*, the only function L' leading to either of these terms is precisely the function L which we have already found. Therefore, in this third case also, it is impossible to get an Eulerian Function of the required form (12).

(4) $\beta=1, \alpha_2=2$. The additional conditions are here

$$\alpha=\alpha_1=\alpha_3=\beta_1=\beta_2=\beta_3=\gamma_1=\gamma_3=0, \quad \gamma=1, \quad \gamma_2=-1.$$

Hence

$$L = \frac{vwu_2^2}{w_2}$$

and

$$\text{E.F.} = 2vu_2 - 2 \frac{vwu_2}{w_2^2} w_{22} + 2 \frac{vw}{w_2} u_{22} + 2 \frac{wu_2 v_2}{w_2}.$$

Here we have three extraneous terms. To the first two we apply the same argument as we did in case (3), and conclude that in this case also it is impossible to get an Eulerian Function of the form (12).

Collecting the results of the four possible cases, we may conclude that with a Lagrangian function of the form (13) it is impossible to get an Eulerian Function of the form (12). This result can at once be somewhat generalized as follows. It is obvious that it is impossible to get an Eulerian Function of the form (12) from a Lagrangian function composed of any sum of terms of the form (13). If, now, we define a new variable,

$$z = u^{\alpha} v^{\beta} w^{\gamma} u_1^{\alpha_1} u_2^{\alpha_2} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3},$$

then for any function

$$L = L(u, v, \dots, w_2, w_3),$$

which has no singularity inside the volume region under consideration, a series

$$S = \sum_{-\infty}^{\infty} c_i z^i$$

can be found which converges uniformly to the function L inside the region. But we have seen that no Lagrangian function of the form $\sum c_i z^i$ satisfies our condition of leading to an Eulerian Function of the form (12). Hence no

Lagrangian function of the form (11), which has no singularities in the region considered, can be found which satisfies our condition. But Lagrangian functions involving singularities inside the region in which the fluid motion is taking place are ruled out for physical reasons. Finally, by cyclic substitution we find that all of the above results are valid when any of the expressions of (10) are substituted for vu_2 if only we use the Eulerian equation corresponding. Hence the theorem stated in the introduction has been proved. We shall here restate it in a different form, employing the conditions mentioned in the first section.

"It is impossible to derive the equations of steady motion of a viscous, incompressible fluid from a variation principle involving as Lagrangian function an expression in the velocity components and their first-order space derivatives, unless conditions are imposed on these velocity components such that all of the terms $vu_2, wu_3, wv_3, uv_1, uv_1, vw_2$ disappear from their positions in the Navier-Stokes equations." This disappearance may arise either because the terms vanish identically, or because they are replaced (according to the imposed conditions) by other expressions not so intractable. We shall refer to cases in which such conditions are satisfied as "exceptional cases." It should be noticed that the equations of motion may still be deduced from our variation principle, even though the intractable terms appear, if the latter occur in other of the component Navier-Stokes equations from those which they occupy in general. For example, if our imposed conditions allowed us to replace vu_2 by uv_1 in the x -component Navier-Stokes equation, then the function $L = uvu_1$, substituted in the Eulerian Function corresponding to this x -component, *i. e.* in

$$\frac{\partial}{\partial x} \left(\frac{\partial L}{\partial u_1} \right) + \frac{\partial}{\partial y} \left(\frac{\partial L}{\partial u_2} \right) + \frac{\partial}{\partial z} \left(\frac{\partial L}{\partial u_3} \right) - \frac{\partial L}{\partial u},$$

would give the "intractable" term uv_1 . However, such examples still fall under the class of "exceptional cases," for some imposed condition on the velocities is necessary in order to transform the equations of motion into a form in which they may be deduced from our variation principle.

The above theorem may also be formulated from the point of view of a minimum instead of a variation principle: "Except in the 'exceptional cases' there is no function of the velocity components, their first-order space derivatives (and possibly the space coordinates), which is a minimum for the steady motion of a viscous, incompressible fluid."

We proceed with a discussion of various examples of the "exceptional cases" for which steady solutions have been found. There are essentially only three such cases existing for viscous fluids. One is motion in which the entire fluid moves as a rigid body with uniform rotation. In this case we may write

$$u = cy, \quad v = -cx,$$

so that

$$2vu_2 = -2vv_1 = -\frac{\partial}{\partial x}(v^2) = -\frac{\partial}{\partial x}(u^2 + v^2) = -\frac{\partial}{\partial x}q^2,$$

$$2uv_1 = -2uu_2 = -\frac{\partial}{\partial y}q^2,$$

$$\therefore (\mathbf{q} \cdot \nabla) \mathbf{q} = -\frac{1}{2} \nabla q^2,$$

and we have the particular example of an "exceptional case" previously discussed explicitly. The second case includes plane laminar flow and Poiseuille flow in a tube of uniform cross-section. In both of these cases we can choose a set of rectangular axes such that two components of velocity vanish throughout the fluid. Hence we have the exceptional case in which the intractable terms vanish identically. Finally, there is Hamel's case of flow in logarithmic spirals, which will be discussed in detail in section 5. Here there is only one non-vanishing component of velocity relative to a set of orthogonal curvilinear coordinates, and in the one component Navier-Stokes equation which remains to determine the velocity, the component of $(\mathbf{q} \cdot \nabla) \mathbf{q}$ is replaced by the corresponding component of $\frac{1}{2} \nabla q^2$, so that the "exceptional case" is similar to that explicitly mentioned immediately following equation (9).

Hence all of the cases of steady motion thus far discovered belong to the class of "exceptional cases," and it should be possible to find Lagrangian functions for all of them.

3. *The Lagrangian Functions for Plane Laminar and Poiseuille Flow.*

For the discussion of plane laminar flow we choose Cartesian coordinates and assume two-dimensional motion, writing

$$w = \frac{\partial}{\partial z} = 0.$$

In general it will be convenient, when discussing two-dimensional motion, to retain the three-dimensional language

as to volume and surface elements, introducing a unit length in the z direction to complete the three dimensions ; *i. e.*,

$$d\tau = dx dy . 1,$$

$$\int_s ds = \text{line integral in the } x, y \text{ plane.}$$

We consider flow between two parallel walls $x=x_1$ and $x=x_2$, and take a region bounded by these two walls and any two perpendicular planes $y=y_1$ and $y=y_2$ (and by two planes $z=z_1$ and $z=z_2$ unit distance apart). Then, introducing the usual restriction on the motion,

$$q = u, \quad v = 0,$$

and the continuity equation gives

$$u_1 = 0 \quad \text{or} \quad u = u(y).$$

The Navier-Stokes equations reduce to the following single equation for the determination of u in terms of the pressure gradient :

$$\bar{\mu} u_{22} - \frac{\partial p}{\partial x} = 0. \quad . \quad . \quad . \quad . \quad (16)$$

In this case the flux of kinetic energy out of our region is zero, *i. e.* $R=0$. Hence the equation of conservation of energy takes Helmholtz's simplified form (see equation (5)) :

$$P - Q = 0,$$

and we expect Helmholtz's result to hold, namely

$$\delta(P - \frac{1}{2}Q) = 0.$$

This equation is found to be valid ; in fact Rayleigh has shown* that Q is an absolute minimum. However, if we take the dissipation function Φ as Lagrangian function, we do not get the equation of motion (16) from our variation principle.

In order to find the proper Lagrangian function we must somewhat alter the procedure followed in section 2. The difficulty is that here we have already introduced the continuity equation explicitly, and consequently cannot introduce an arbitrary multiplier λ into the variation equation, which multiplier is later to be identified with the pressure p . We must find some other way of bringing p into the Lagrangian function. The method adopted appears

* *Loc. cit.*

to be the one which must be employed in general, whenever the continuity equation has been explicitly used to restrict the nature of the velocity components. The method is the following. Instead of considering P as a surface integral and as having, therefore, no effect on the variation problem, we transform P to a volume integral, just as we previously transformed R , and incorporate the "density function" \mathbf{P} in the Lagrangian function. Since at the walls the velocity is zero, according to the customary assumption of no slip, there is no work done on the fluid in our region due to viscous forces acting across these boundaries. Obviously no work is done by any tractions across the planes $z=z_1$ and $z=z_2$. Since the velocity is normal to the other boundaries $y=y_1$ and $y=y_2$, the only work done on the region is due to pressure forces, and we may write (\mathbf{n} =outwardly drawn normal),

$$P = - \int_S \mathbf{p} \mathbf{n} \cdot \mathbf{q} \, ds = - \int_S \mathbf{n} \cdot \mathbf{p} \mathbf{q} \, ds,$$

and applying the divergence theorem

$$P = - \int_V \nabla \cdot \mathbf{p} \mathbf{q} \, d\tau = - \iiint \frac{\partial}{\partial x} (p u) \, dx \, dy,$$

and, finally, since $u=u(y)$,

$$P = - \int_V u \frac{\partial p}{\partial x} \, d\tau,$$

$$\therefore \mathbf{P} = -u \frac{\partial p}{\partial x}.$$

From equation (4)

$$\Phi = \mu u_2^2,$$

and hence the variation principle (6) becomes for this case

$$\left. \begin{array}{l} \delta(P - \frac{1}{2}Q) = 0 \\ \text{or} \end{array} \right\} \quad \delta \iiint_V \left\{ \frac{\mu}{2} u_2^2 + u \frac{\partial p}{\partial x} \right\} \, dx \, dy = 0. \quad (17)$$

The Eulerian equation gives

$$\mu u_{22} - \frac{\partial p}{\partial x} = 0,$$

which is exactly the equation of motion (16).

Hence for plane laminar flow we have verified the fact that the correct Lagrangian function, giving the equations of motion by a variation principle, is

$$L = \mathbf{P} - \frac{1}{2}\Phi - \mathbf{R}, \quad . \quad . \quad . \quad . \quad (18)$$

in agreement with (6). In this particular case, since $\mathbf{R}=0$, we have

$$L_{\text{plane laminar}} = \mathbf{P} - \frac{1}{2}\Phi. \quad . \quad . \quad . \quad (19)$$

The case of Poiseuille flow in a tube is obviously exactly the same in principle as the above. The imposed conditions imply that all but one component of velocity vanish, so that if the x axis is parallel to the axis of the tube,

$$q = q_x = u.$$

Then the continuity equation imposes the additional restriction that u is independent of x and is a function of a single parameter of the nature of the distance from the axis, so that the Navier-Stokes equations reduce to a single one determining u as a function of this parameter. \mathbf{R} vanishes exactly as above, and \mathbf{P} has obviously the same value:

$\mathbf{P} = -u \frac{\partial p}{\partial x}$, so that the only problem in finding L is to express Φ in the proper coordinates. In the case of a circular tube, for example, where we define r as the distance from the axis,

$$u = u(r),$$

$$\Phi = \mu \left(\frac{\partial u}{\partial r} \right)^2,$$

and

$$L = \mathbf{P} - \frac{1}{2}\Phi = - \left\{ \frac{1}{2}\mu \left(\frac{\partial u}{\partial r} \right)^2 + u \frac{\partial p}{\partial x} \right\}.$$

Hence the variation principle takes the form :

$$\delta \int_V L d\tau = \delta \int_0^{2\pi} \int_{x_1}^{x_2} \int_0^{r_0} \left\{ \frac{1}{2}\mu \left(\frac{\partial u}{\partial r} \right)^2 + u \frac{\partial p}{\partial x} \right\} r dr dx d\theta = 0,$$

where r_0 =radius of the tube, or

$$2\pi(x_2 - x_1) \delta \int_0^{r_0} \left\{ \frac{\mu r}{2} \left(\frac{\partial u}{\partial r} \right)^2 + ur \frac{\partial p}{\partial x} \right\} dr = \delta \int_0^{r_0} L_0 dr = 0,$$

where

$$L_0 = 2\pi(x_2 - x_1)rL.$$

The Eulerian equation (writing $u' = \frac{\partial u}{\partial r}$)

$$\frac{\partial}{\partial r} \left(\frac{\partial L_0}{\partial u'} \right) - \frac{\partial L_0}{\partial u} = 0$$

gives

$$\mu \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right) - r \frac{\partial p}{\partial x} = 0$$

or

$$\frac{1}{\mu} \frac{\partial p}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right),$$

which is exactly the Navier-Stokes equation for $u(r)$.

Hence the results of this case are identical with those for the previous one as far as the form of the Lagrangian function is concerned. A new element which has appeared, however, is one which we shall find again in section 5, namely: if curvilinear coordinates are employed then, in writing the Eulerian equations, the functions of coordinates introduced through the transformation from a Cartesian to a curvilinear system, must be taken into account.

The results of this section have been to verify, for some special cases, the correctness of the variation principle given in (6), and to demonstrate the fact that if the continuity equation be introduced to give an explicit limitation on the velocity components, then, in getting the Lagrangian function, P must be considered as a volume integral and must be included in performing the variations.

4. Certain Vector and Curvilinear Coordinate Relations.

In this section a few relations are given, both because they are required for the analysis of the subsequent section and also because they have a certain amount of interest *per se*. As mentioned in the introduction, it is convenient to change notation at this point, using u, v, w to denote families of orthogonal curvilinear coordinates, while the corresponding velocity components are given by q_u, q_v, q_w . In terms of Cartesian coordinates we have

$$u = u(x, y, z); \quad v = v(x, y, z); \quad w = w(x, y, z).$$

Then, if ds represents the line element, we define the quantities U, V, W by

$$ds^2 = U^2 du^2 + V^2 dv^2 + W^2 dw^2,$$

where

$$U = U(u, v, w); \quad V = V(u, v, w); \quad W = W(u, v, w).$$

Then the volume element becomes

$$d\tau = UVW \, du \, dv \, dw.$$

Unit vectors in the directions of increasing u, v, w respectively are denoted by $\mathbf{i}_u, \mathbf{i}_v, \mathbf{i}_w$ (at any point u, v, w in the space). The expressions for $\nabla\phi$, $\nabla \cdot \mathbf{A}$, $\nabla^2\phi$, and $\nabla \times \mathbf{A}$,

where ϕ represents an arbitrary scalar and \mathbf{A} an arbitrary vector, in terms of such a coordinate system, are given in many standard mathematical and physical works. In addition to these we shall require the curvilinear coordinate expressions for $\nabla^2 \mathbf{A}$ and $(\mathbf{A} \cdot \nabla) \mathbf{A}$. By elementary vector analysis these may be deduced from the above-mentioned standard expressions. The following formulæ, which the author has been unable to find in any work with which he is acquainted, have been obtained in this way:—

$\nabla^2 \mathbf{A}$

$$\begin{aligned}
 &= \left\{ \frac{1}{U} \frac{\partial}{\partial u} (\nabla \cdot \mathbf{A}) + \frac{1}{VW} \left[\frac{\partial}{\partial w} \left\{ \frac{V}{WU} \left(\frac{\partial U A_u}{\partial w} - \frac{\partial W A_w}{\partial u} \right) \right\} \right. \right. \\
 &\quad \left. \left. - \frac{\partial}{\partial v} \left\{ \frac{W}{UV} \left(\frac{\partial V A_v}{\partial u} - \frac{\partial U A_u}{\partial v} \right) \right\} \right] \right\} \mathbf{i}_u \\
 &+ \left\{ \frac{1}{V} \frac{\partial}{\partial v} (\nabla \cdot \mathbf{A}) + \frac{1}{WU} \left[\frac{\partial}{\partial u} \left\{ \frac{W}{UV} \left(\frac{\partial V A_v}{\partial u} - \frac{\partial U A_u}{\partial v} \right) \right\} \right. \right. \\
 &\quad \left. \left. - \frac{\partial}{\partial w} \left\{ \frac{U}{VW} \left(\frac{\partial W A_w}{\partial v} - \frac{\partial V A_v}{\partial w} \right) \right\} \right] \right\} \mathbf{i}_v \\
 &+ \left\{ \frac{1}{W} \frac{\partial}{\partial w} (\nabla \cdot \mathbf{A}) + \frac{1}{UV} \left[\frac{\partial}{\partial v} \left\{ \frac{U}{VW} \left(\frac{\partial W A_w}{\partial v} - \frac{\partial V A_v}{\partial w} \right) \right\} \right. \right. \\
 &\quad \left. \left. - \frac{\partial}{\partial u} \left\{ \frac{V}{WU} \left(\frac{\partial U A_u}{\partial w} - \frac{\partial W A_w}{\partial u} \right) \right\} \right] \right\} \mathbf{i}_w,
 \end{aligned}$$

$(\mathbf{A} \cdot \nabla) \mathbf{A}$

$$\begin{aligned}
 &= \left\{ \frac{1}{2U} \frac{\partial A^2}{\partial u} - \frac{A_u}{UV} \left(\frac{\partial V A_v}{\partial u} - \frac{\partial U A_u}{\partial v} \right) \right. \\
 &\quad \left. + \frac{A_w}{WU} \left(\frac{\partial U A_u}{\partial w} - \frac{\partial W A_w}{\partial u} \right) \right\} \mathbf{i}_u \\
 &+ \left\{ \frac{1}{2V} \frac{\partial A^2}{\partial v} - \frac{A_v}{VW} \left(\frac{\partial W A_w}{\partial v} - \frac{\partial V A_v}{\partial w} \right) \right. \\
 &\quad \left. + \frac{A_u}{UV} \left(\frac{\partial V A_v}{\partial u} - \frac{\partial U A_u}{\partial v} \right) \right\} \mathbf{i}_v \\
 &+ \left\{ \frac{1}{2W} \frac{\partial A^2}{\partial w} - \frac{A_w}{WU} \left(\frac{\partial U A_u}{\partial w} - \frac{\partial W A_w}{\partial u} \right) \right. \\
 &\quad \left. + \frac{A_v}{VW} \left(\frac{\partial W A_w}{\partial v} - \frac{\partial V A_v}{\partial w} \right) \right\} \mathbf{i}_w.
 \end{aligned}$$

. . . (20)

Using the above formulæ it is easy to express the Navier-Stokes equations in terms of any curvilinear orthogonal coordinate system. However, in searching for Lagrangian functions it is necessary to have the dissipation function Φ expressed in a similar way. The simplest method of accomplishing this appears to be to first obtain an expression for Φ involving only vectors, and hence entirely independent of coordinate systems, and then to use the above transformation formulæ to get the final form desired. There is also some interest for other purposes in having an expression for Φ independent of any coordinate system. The calculation of the transformation from the Cartesian form of (4) to the vector form is somewhat lengthy, so that only the final result, which can immediately be verified, is given here * :

$$\Phi = \mu \{ \nabla^2 q^2 - (\nabla \times \mathbf{q})^2 - 2\mathbf{q} \cdot \nabla^2 \mathbf{q} \}. \quad . \quad (21)$$

It should be noted that the condition of incompressibility has not been introduced in the derivation of this expression, so that it is valid for any viscous fluid.

5. *The Lagrangian Function for Logarithmic Spiral Flow.*

In a recent paper† Hamel has given a very elegant discussion of a new general type of steady motion of an incompressible fluid. He considers a two-dimensional motion in which the streamlines are restricted to coincide with an isometric family of curves. He then proves that this family must necessarily be a set of logarithmic spirals. In discussing this type of motion here it is convenient to employ a notation different from that of Hamel, which was used by the present writer in some recent work on the same subject‡. This notation is in part identical with that of the previous section.

Since we are dealing with two-dimensional motion, we take

$$\frac{\partial}{\partial w} = 0, \quad W = 1, \quad q_w = 0,$$

and define

$$u + iv = \pi(x + iy) = \pi(z),$$

where π is a function of the complex variable $z = x + iy$.

* The details of the transformation are given in an unpublished thesis by the author; California Institute of Technology, 1928.

† *Deutsche Mathematiker-Vereinigung*, xxv. p. 34.

‡ Appearing in a current issue of the *Mathematische Annalen*.

This imposes the restriction $V=U$, and implies that $u=\text{constant}$ and $v=\text{constant}$ constitute two orthogonal families of isometric curves. We assume that the velocity of the fluid is everywhere tangent to the family $u=\text{constant}$, *i. e.* the streamlines coincide with this family.

$$\therefore q = q_u, \quad q_v = 0.$$

The continuity equation for an incompressible fluid gives at once

$$q = \frac{f(v)}{U},$$

where f is an arbitrary function of v . Introducing all of these restrictions, and using equations (20), the Navier-Stokes equations (1) for this case reduce to

$$\left. \begin{aligned} \frac{\partial p}{\partial u} &= -\frac{\rho}{2} f^2 \frac{\partial}{\partial u} (1/U^2) + \mu \frac{\partial}{\partial v} (f'/U^2), \\ \frac{\partial p}{\partial v} &= -\frac{\rho}{2} f^2 \frac{\partial}{\partial v} (1/U^2) - \mu f' \frac{\partial}{\partial u} (1/U^2), \end{aligned} \right\} \quad \dots \quad (22)$$

where primes denote differentiation with respect to v .

In the work cited above it is proved from these equations that the curves $u=\text{constant}$ and $v=\text{constant}$ must necessarily coincide with the following orthogonal families of logarithmic spirals:

$$\left. \begin{aligned} u &= b \log r - a\theta, \\ v &= a \log r + b\theta, \end{aligned} \right\} \quad \dots \quad (23)$$

where r, θ are polar coordinates and a, b are arbitrary real constants. Plane radial and Couette flow are given as the two limiting cases for $a=0$ and $b=0$ respectively. It is convenient to introduce two new real constants A and B , where

$$A = \frac{2b}{a^2 + b^2}, \quad B = \frac{2a}{a^2 + b^2}.$$

Then it has been shown that

$$U^2 = e^{Au+Bv} \quad \dots \quad (24)$$

The differential equation for f , which might be called the equation of motion, is obtained by eliminating p from equations (22) and substituting the above value of U^2 into the resulting equation. This gives

$$A\rho f f' + \mu \{ (A^2 + B^2) f' - 2B f'' + f''' \} = 0,$$

or integrating once and writing $\frac{\mu}{\rho} = \nu =$ coefficient of kinematic viscosity,

$$f'' - 2Bf' + (A^2 + B^2)f + \frac{A}{2\nu}f^2 = \alpha, \quad (25)$$

where α is an arbitrary constant of integration.

The problem is now to find a Lagrangian function which will give the "equation of motion" (25) through the application of a variation principle. For the region over which to integrate we make a similar choice to that of section 3, *i. e.* we take z boundaries unit distance apart. We consider flow between fixed walls which coincide with two members of the chosen family of logarithmic spirals, and take these two walls $u = u_1$ and $u = u_2$ as boundaries of our region. The other two boundaries are formed by any two members of the orthogonal family of curves, $v = v_1$ and $v = v_2$. Notice that in any particular problem u_1 and u_2 are specified, while v_1 and v_2 are arbitrary. We assume $\delta q = 0$ at all these boundaries and search for a Lagrangian function L such that, if we set

$$\delta \int_V L d\tau = 0,$$

where V is the region specified, then the Eulerian equation is (25). From the general results of the first section it is to be expected that the variation principle will be of the form *i. e.* (6),

$$\delta \int_V L d\tau \stackrel{?}{=} \delta(P - \frac{1}{2}Q - \gamma R). \quad (26)$$

However, in connexion with this particular case two remarks must be made. First, since the continuity equation has been explicitly introduced in the expression for velocity components, we expect from section 3 that P must be considered as a volume integral and included in the variation. Second, since we have chosen a particular set of coordinates, and since this choice has introduced certain restrictions, we may expect certain functions of the coordinates to appear in the right-hand member of (26). For the same reason the numerical factor γ , which appears in that member, may not be unity, as was found in the second section to be the case in general. For these reasons it will be convenient to first try

$$L = L' \equiv P - \frac{1}{2}\Phi - \gamma R, \quad (27)$$

remembering that it may be necessary to introduce some function of the coordinates into the right-hand member in

order that the Eulerian equation give the equation of motion (25).

In evaluating \mathbf{P} , the conditions are essentially the same as for plane laminar flow, and for the same reasons as mentioned in section 3 the work of the external forces is entirely due to pressure forces. (Notice that the velocity is perpendicular to the boundaries $v=v_1$ and $v=v_2$.) As in that section, we retain the three-dimensional language, but omit the z variable as having no effect on the equations. Hence

$$\begin{aligned} \mathbf{P} &= - \int_{\mathbf{s}} p \mathbf{n} \cdot \mathbf{q} \, ds = - \int_{\mathbf{v}} \mathbf{q} \cdot \nabla p \, d\tau, \\ \mathbf{P} &= - \mathbf{q} \cdot \nabla p = - q_u \frac{1}{U} \frac{\partial p}{\partial u}, \\ \therefore \quad \mathbf{P} &= - \frac{f}{U^2} \frac{\partial p}{\partial u} \quad . \quad . \quad . \quad . \quad . \quad (28) \end{aligned}$$

Since the pressure p has been eliminated in the equation of motion (25) which we are trying to obtain, and the arbitrary constant α has been introduced, hence in (28) we must replace $\frac{\partial p}{\partial u}$ by an expression involving the velocity, its first derivatives, and α . To do this we go back to the equations of motion as given in (22). Here $\frac{\partial p}{\partial u}$ is given in terms of f and f'' . The f'' is eliminated by using (25). Eliminating f'' in this way and introducing the value for U^2 given in (24), we get

$$\frac{\partial p}{\partial u} = - \frac{\mu}{U^2} \{ (A^2 + B^2) f - B f' - \alpha \},$$

so that, finally,

$$\mathbf{P} = \frac{\mu}{U^4} \{ (A^2 + B^2) f^2 - B f f' - \alpha f \}. \quad . \quad . \quad (29)$$

The general expression for \mathbf{R} given in (8) holds in this case, so that

$$\begin{aligned} \mathbf{R} &= \frac{\rho}{2} \mathbf{q} \cdot \nabla q^2 = \frac{\rho}{2} \frac{f}{U^2} \frac{\partial}{\partial u} \left(\frac{f^2}{U^2} \right) = \frac{\rho}{2 U^2} f^3 \frac{\partial}{\partial u} \left(\frac{1}{U^2} \right), \\ \therefore \quad \mathbf{R} &= - \frac{1}{U^4} \frac{\rho}{2} A f^3. \quad . \quad . \quad . \quad . \quad (30) \end{aligned}$$

Using the standard transformation formulæ and equations (20) to express Φ as given in (21) in terms of our

particular coordinate system, we have, after a little calculation,

$$\Phi = \frac{\mu}{U^4} \{ (A^2 + B^2) f^2 - 2Bff' + f'^2 \}. \quad (31)$$

Hence, from (27),

$$L' = e^{-2(Au+Bv)} \left\{ \mu \left(\frac{A^2 + B^2}{2} f^2 - \alpha f - \frac{1}{2} f'^2 \right) + \frac{\gamma}{2} \rho A f^3 \right\}. \quad (32)$$

We remarked in section 3 that it was necessary to form a function L_0 (obtained by multiplying L by the Jacobian of the transformation from Cartesian to curvilinear coordinates) to use instead of L in setting up the Eulerian equation. This is a general rule for carrying out a variation principle in any curvilinear coordinates. In our case we have

$$\delta \int_V L d\tau = \delta \int \int_V L U^2 du dv = \delta \int \int_V L_0 du dv = 0,$$

and the Eulerian equation is

$$\frac{\partial}{\partial v} \left(\frac{\partial L_0}{\partial f'} \right) - \frac{\partial L_0}{\partial f} = 0.$$

If we take $L=L'$ as defined in (32), this does not give the equation of motion (25), and it appears that, in order to get the result we are seeking, we must set

$$L = \frac{L'}{U^2}. \quad (33)$$

Then $L_0 = LU^2 = L'$, and the Eulerian equation becomes

$$\frac{\partial}{\partial v} \left(\frac{\partial L'}{\partial f'} \right) - \frac{\partial L'}{\partial f} = 0,$$

which gives

$$f'' - 2Bf' + (A^2 + B^2)f + \frac{3\gamma}{2\nu} A f^2 = \alpha,$$

which is exactly the equation of motion (25) if $\gamma = \frac{1}{3}$.

Hence, as we suspected, the introduction of a particular coordinate system may alter the general expression for L . In the case of logarithmic spiral flow this alteration consists in changing L from the invariant function

$$L = \mathbf{P} - \frac{1}{2}\Phi - \gamma\mathbf{R}$$

to the expression depending on the coordinate system

$$L = (\mathbf{P} - \frac{1}{2}\Phi - \gamma\mathbf{R}) \frac{1}{U^2}, \quad (34)$$

where γ has the value $\frac{1}{2}$ instead of 1, and U^2 is the Jacobian of the transformation from Cartesian to logarithmic spiral coordinates.

6. Conclusions.

The results of this paper, in so far as they relate to a variation principle, may be summarized as follows:—

- (1) Except in certain "exceptional cases" the equations of steady motion of a viscous, incompressible fluid cannot be deduced from a variation principle involving a Lagrangian function containing only the velocity components, their first-order space derivatives, and possibly functions of the coordinates.
- (2) All the cases of such motion which have yet been discovered belong to this class of "exceptional cases," and the corresponding variation principles may be found.
- (3) The Lagrangian functions for these cases are exhibited and the corresponding variation principles are found to be all of the form $\delta(P - \frac{1}{2}Q - \gamma R) = 0$, except for functions of coordinates, which may be introduced through the imposing of restrictions on the velocity by the coordinate system chosen to describe the motion.

In conclusion, the author wishes to express his deep appreciation of the continued assistance and inspiration of Prof. H. Bateman, who originally suggested the problem and offered many valuable suggestions during its progress.

Norman Bridge Laboratory,
October 1928.

LXXVIII. *A New Method of Measuring the Electrical Resistances of Alloys.* By A. L. NORBURY, D.Sc., The British Cast-Iron Research Association (Birmingham) *.

Introduction.

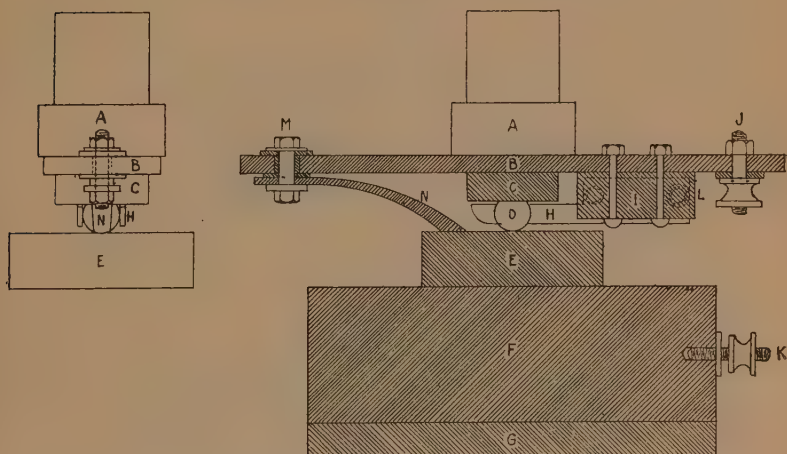
THE present work was commenced with the idea of measuring the diameters of Brinell † impressions, while the load was on, by measuring the electrical resistance of a

* Communicated by the Author.

† The Brinell hardness test consists in pressing a 10-mm. hardened steel ball into the material under test by means of a known load for 30 seconds. The diameter of the resulting impression is measured with a microscope, and the Brinell hardness number is obtained by dividing the load applied by the spherical area of the impression produced.

circuit comprising the Brinell ball and the specimen under test. An increase in the diameter of the impression produced should decrease the electrical resistance of the above circuit; consequently it should be possible to measure diameters in terms of electrical resistance. It was found, however, that the specific electrical resistance of the material tested influenced the results obtained. Consequently the method may be used to measure the specific electrical resistance of alloys by measuring the electrical resistance in the Brinell ball circuit, measuring the diameter of the

Fig. 1 *a*.

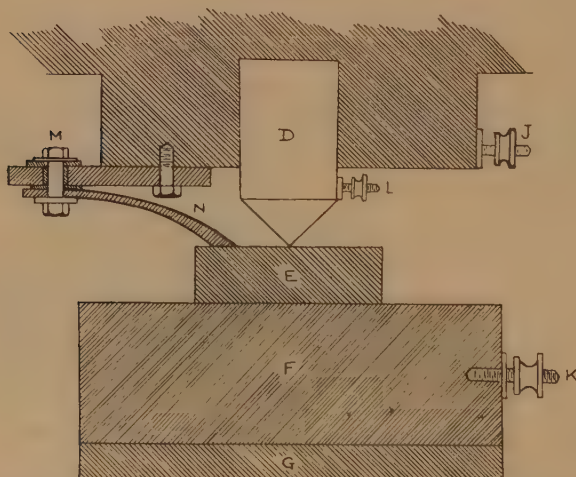


Measurement of drop of potential between equator of 10-mm. ball and surface of specimen.

- A. Mild steel holder for attaching to Brinell machine.
- B. Mild steel plate screwed on to A in fig. 1 *a* and on to Brinell machine in fig. 1 *b*.
- C. Hardened steel disk.
- D. 10-mm. ball-bearing ground flat on top in fig. 1 *a* and a 90° cone in fig. 1 *b*.
- E. Specimen under test.
- F. Mild steel table.
- G. Uralite asbestos sheet insulator.
- H. Two hardened steel strips making contact with 10-mm. ball at its equator.
- I. Vulcanite block for insulating H from B.
- J & K. Terminals for accumulator current.
- L. Terminal for P.D. contact at equator of 10-mm. ball in fig. 1 *a*. Soldered on to shoulder of 90° cone in fig. 1 *b*.
- M. Terminal insulated from B for P.D. contact N.
- N. Cold-hammered copper P.D. contact pressing on to surface of specimen.

impression produced, and interpreting the results by means of calibration curves. Conversely, knowing the specific electrical resistance of the material under test, the size of the Brinell impression can be obtained. Similar tests were carried out, using 90° cones of steel and copper. The method makes it possible to measure the specific electrical resistance of alloys of any shape or size, provided a plane surface about 5 mm. by 5 mm. or larger is available.

The apparatus shown in figs. 1 *a* and 1 *b* was developed for this purpose. A current of 2 or 3 amperes was passed through the circuit, and the drop of potential between the equator of the ball or shoulder of the 90° cone and the

Fig. 1 *b*

Measurement of drop of potential between shoulder of 90° cone and surface of specimen

[For explanation of lettering see fig. 1 *a*.]

surface of the specimen was compared on a Tinsley vernier potentiometer with the drop of potential across a standard resistance in the same circuit.

Elimination of Contact Resistance between Ball and Specimen under Test.

At first very erratic drop of potential results were obtained, due to bad electrical contact, caused by the presence of vaseline, oil, emery powder, etc., between the 10-mm. ball and the impression. With a vaselined ball the drop of

potential was as much as ten times too great, and would gradually decrease with time as the vaseline was squeezed out from between the ball and the impression. Tests were then made on specimens freshly polished with No. 0 emery paper and washed (as was the 10-mm. ball) with methylated spirits. The results obtained in this way were moderately satisfactory, and could be repeated to within about 10 per cent. Further experiments showed that the drop of potential measured as above was still high on account of contact resistance, and that it was necessary to etch the specimen and ball and wash and dry them with methylated spirits just before making an impression. When this was done, very consistent and accurate results were obtained. Etching removed grease, particles of emery, etc., very effectively, and thereby ensured perfect electric contact between the specimen and the impressed Brinell ball.

Electrical Resistance Results, using a 10-mm. Ball.

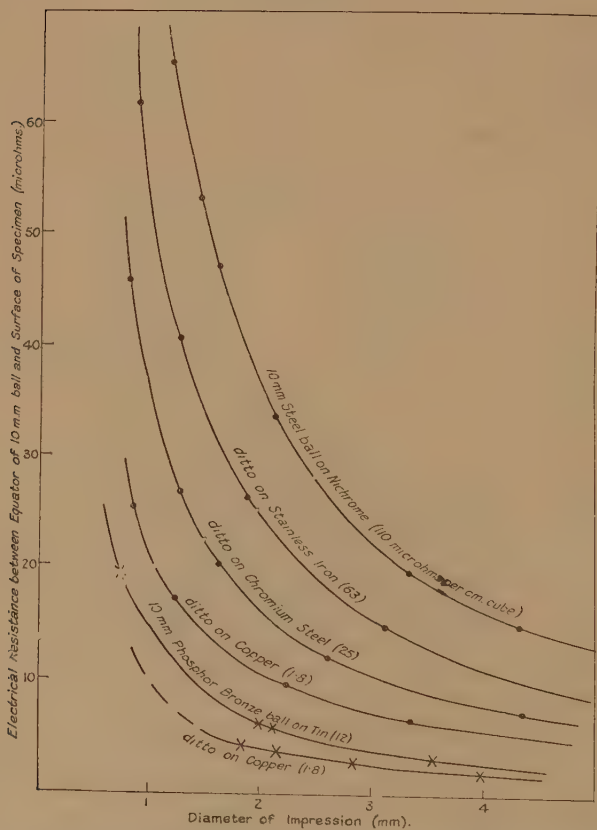
Results obtained on etched surfaces in the above manner are plotted in fig. 2, which shows the measured electrical resistance between the equator of the ball and the surface of the specimen tested, for various-sized impressions, on certain typical materials. (The diameters of the impressions were measured with a travelling microscope in the usual manner.)

The electrical resistances measured are dependent on the diameter of the Brinell impression, on the electrical resistance of the 10-mm. Brinell ball and on the electrical resistance of the material under test. That the last is so will be seen from the specific electrical resistances of the materials tested, which have been written in against each curve in fig. 2.

The two lowest curves in fig. 2 show the results of similar tests on tin and copper, using a 10-mm. phosphor-bronze ball. The electrical resistance of the phosphor-bronze ball, viz., 9 microhms per cm. cube, was considerably lower than that of the hardened steel ball, and consequently the curve showing tests with the phosphor-bronze ball on copper is considerably lower than that for the steel ball on copper. Tests were made which showed that the exact position of the P.D. contact on the surface of the specimen had no measurable effect on the P.D. measured. Tests were made with currents of less than 1 ampere and with currents of over 15 amperes passing through the same small impression (1 to 2 mm. diameter), but any alteration in the resistance results obtained consequent on heating or thermoelectric effects was so small as to be within the limits of experimental error.

Similarly, the hardness of the specimen tested had no measurable influence on the results obtained, since the Brinell numbers (10 mm./3000 kg./30 sec.) of the specimens shown in fig. 2 were as follows: cold-hammered copper 90, chromium steel 190, stainless iron 400, nichrome 200. Furthermore,

Fig. 2.



Electrical resistance between equator of 10-mm. ball and surface of specimen. Plotted against diameter of impression on materials of different electrical resistances.

a test made on tin 4 fell into line, according to the electrical resistance of tin, between the results plotted in fig. 2 for copper and chromium steel.

If the results of fig. 2 are plotted logarithmically, they fall

on straight lines according to the following equation (which does not, however, hold for large-diameter impressions):

$$\log \text{E.R.} = \log a + n \log d,$$

$$\therefore \text{E.R.} = ad^n,$$

where E.R.=electrical resistance between equator of 10-mm. ball and surface of specimen; d =diameter of impression produced; and a and n are two constants, each depending in value on the electrical resistance of the material tested plus that of the 10 mm.-ball. The equation is similar in form to Meyer's formula, showing the relationship between the load applied and diameter of impression produced in the Brinell test.

Electrical Resistance Results, using 90° Cones.

Results were obtained in a similar manner, using a 90° steel cone, as shown in fig. 1 *b*, instead of a 10-mm. ball. The top drop of potential contact (equivalent to H in fig. 1) was soldered on to the shoulder of the 90° cone. If the electrical resistances measured are plotted against the reciprocals of the diameters of the impressions produced, as has been done in fig. 3 *a*, a linear relationship is obtained for each material, and, as before, the results are dependent on the specific electrical resistance of the material under test. The specific electrical resistances of the materials under test are written in against the appropriate lines in figs. 3 *a* and 3 *b*. Fig. 3 *b* shows similar tests, using a 90° copper cone instead of a steel cone. It will be noted that only soft materials (*e.g.*, tin and lead and their alloys, the latter being specially made for the present purpose) could be tested with the relatively soft copper cone.

It will be seen in figs. 3 *a* and 3 *b* that the lines meet at a point corresponding with zero electrical resistance and a diameter of impression equal to about 50 mm. This is approximately the diameter of impression that would have been obtained if it had been possible to immerse the 90° cone up to the top drop of potential contact, which was 3 mm. or 4 mm. up from the shoulder on the 25-mm. diameter cylindrical part.

It will also be seen that the resistances obtained with the copper cone in fig. 3 *b* are in all cases lower, for equal diameter impressions, than those obtained with the hardened steel cone (fig. 3 *a*) on the same materials. The difference is due—as before—to the lower electrical resistance of the copper cone. The results in figs. 3 *a* and 3 *b* are compared in fig. 4, where the electrical resistances measured for 1 mm.

Fig. 3 b.

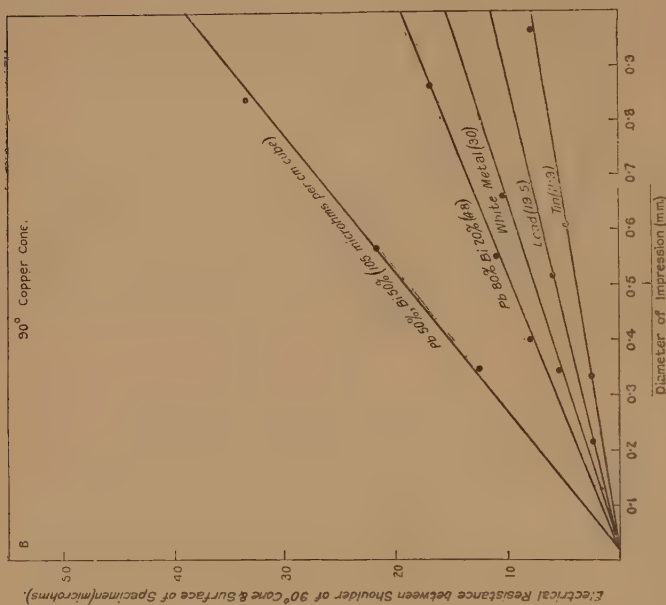
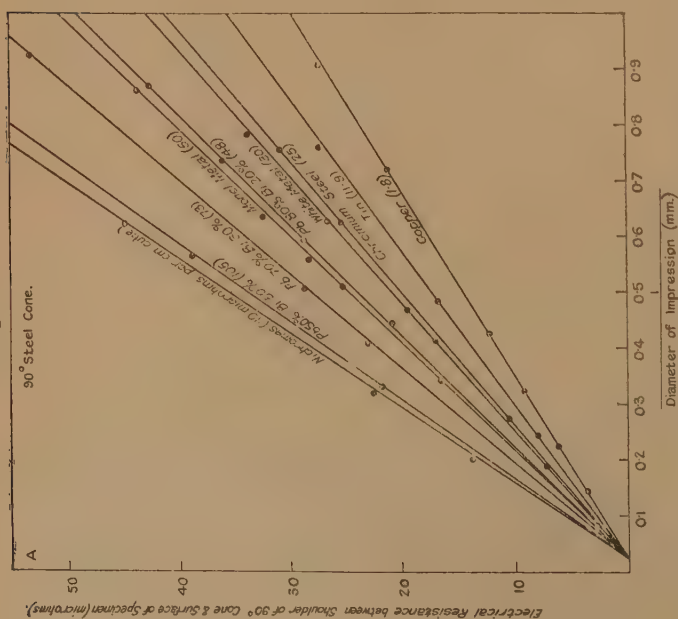


Fig. 3 a.

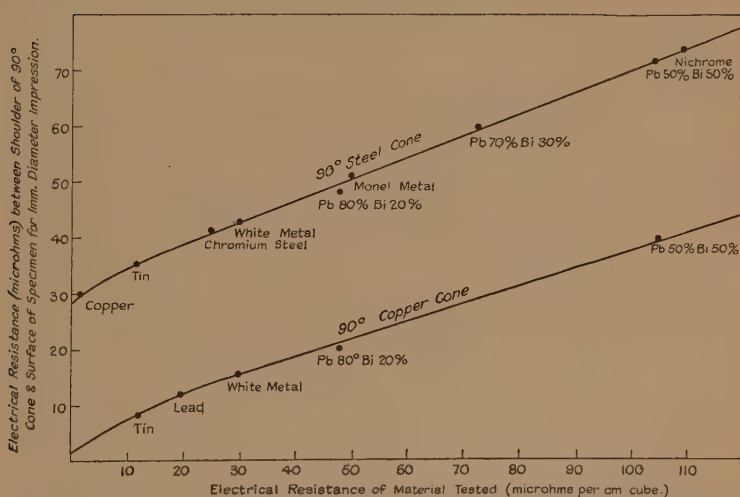


Electrical resistance between shoulder of 90° cone and surface of specimen. Plotted against diameter of impression for various-sized impressions on various materials, using in Fig. 3 a a 90° steel cone and in Fig. 3 b a 90° copper cone.

diameter impressions on various materials have been plotted against the specific electrical resistances of the materials. This figure shows that the results are directly dependent on the specific electrical resistance of the material under test and on the specific electric resistance of the material used in the 90° cone.

In view of the exact dependence of the results on the specific electrical resistance of the material under test, it is possible to use the method to measure this property of alloys. The method has certain advantages, since it can be applied to pieces of any shape or size without any machining other than filling a flat surface about 5 mm. by 5 mm. or larger.

Fig. 4.



Electrical resistances (microhms) in 90° cone circuit for 1-mm. diameter impressions on various materials plotted against the electrical resistances of the materials tested.

As an instance—the specific electric resistances of 60/40 brass and phosphor-bronze 10-mm. balls were measured by the above method by filling small flat surfaces on them and testing them, as above, with a 90° steel cone and interpreting the results obtained in terms of figs. 3 a and 4.

In conclusion the author wishes to thank Principal C. A. Edwards, D.Sc., for facilities for carrying out the present work in his department at Swansea and for his encouragement and interest, and Dr. L. B. Pfeil for drawing fig. 1 and for many helpful suggestions.

LXXIX. *On the Separation of Thorium from Uranium by means of Ether.* By PAUL MISCIATTELLI, D.Phil. (lately Ramsay Memorial Fellow, University of Oxford)*.

THE method of separating uranium from thorium by extracting the nitrates with ether has been the subject of divergent results, some workers finding that it is useless in presence of thorium, which is also extracted by the ether, and others that the separation is effective if the salts are well dried and the ether pure and anhydrous. The present research was undertaken to throw light on this question. It deals with the ternary system— $\text{UO}_2(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_4$, ether—in absence of water. The results for the quaternary system, including water, will form the subject of a separate communication.

The matter is of considerable interest on account of the isotopy of thorium and uranium X. Uranium X was discovered in 1900 by Sir William Crookes† by dissolving crystallized uranyl nitrate in ether, whereby the uranium dissolved in the ethereal layer is entirely free from uranium X, and the latter is wholly contained in that part of the uranium dissolved in the aqueous layer formed by the water of crystallization. The extremely sharp and certain separation of what, chemically, is an infinitesimal trace of thorium from uranium by this method in presence of water is very notable. In 1908 Boltwood‡, for the analysis of many minerals containing uranium and thorium, including thorianite, in which the latter element predominates, successfully used the ether method, extracting the bulk of the uranium from the dried nitrates with anhydrous ether, leaving the thorium nitrate undissolved. But Soddy and Pirret§ found the method perfectly useless for thorianite, and stated that the ether extract contained more thorium than uranium. Mlle Gleditsch||, on the contrary, used the method with success, and stated that she had never observed that the thorium dissolved in the ether if the salts were well dried and the ether pure and dry. The discrepancy was examined by Fleck¶, who stated that the separation, both

* Communicated by Prof. F. Soddy, F.R.S.

† Sir William Crookes, *Proc. Roy. Soc.* lxvi. p. 409 (1900).

‡ B. Boltwood, *Am. J. Sci.* xxv. p. 269 (1908).

§ F. Soddy and Miss Ruth Pirret, *Phil. Mag.* [6] xx. p. 345 (1910).

|| Mlle Gleditsch, *Le Radium*, viii. p. 256 (1911).

¶ A. Fleck, *Trans. Chem. Soc.* ciii. p. 384 (1913).

when anhydrous and in presence of water, is only complete when small quantities—less than 10 per cent.—of thorium are present. In a mixture containing equal quantities of each salt considerable quantities of thorium dissolved in the ether. He used uranium X as an indicator of thorium, and extracted an aqueous solution, proving that the above separation of Crookes fails if thorium is added in sufficient quantity.

In order to throw light upon these apparent contradictions, the ternary system has been systematically examined and the solubility at different temperatures of the anhydrous thorium and uranyl nitrates in anhydrous ether found in presence of one or other, or of both the solid phases. The results are represented in the usual manner by triangular diagrams.

The solubilities were determined by shaking the solutions in presence of excess of one or both solid salts in a large test-tube placed in a Dewar vessel containing melting ice, or in a thermostat at the required temperature. Portions of the solution and of the wet solid were weighed in weighing bottles and separately analysed.

The ether was removed by distillation after the addition of water, to prevent explosions. The cold nearly neutral solution was precipitated by a boiling oxalic acid solution added drop by drop, avoiding an excess that might interfere with the subsequent precipitation of the uranium. The thorium oxalate was ignited and weighed as oxide in the usual manner. The uranium was precipitated from the filtrate by ammonia as ammonium uranate and ignited to constant weight and weighed as U_3O_8 . The filtrate was evaporated to dryness, and any uranium, not precipitated in the first precipitation, recovered and added to the main quantity. From the results the weights of the anhydrous nitrates in the mixtures were calculated, that of the ether being determined by difference.

The results for the solubilities at 0° are shown in Table I. and reproduced in the diagram (fig. 1). The first three columns show the percentages of the three components in the saturated solution, the next three the percentages in the wet residue, and the last column the nature of the solid phase in contact with the solution.

These results show that the solubility of uranyl nitrate in anhydrous ether is increased by the addition of thorium nitrate from 22 to 24 per cent. at 0° . The solution saturated with respect to both salts contains 24 per cent. of the former and 3.4 per cent. of the latter. So that under these

conditions the method would fail as a means of separating uranium and thorium for analysis.

A series of measurements were next done to see how the composition of the solution saturated with respect to both salts varied with temperature. The results are given in Table II. and are also shown in the diagram (fig. 1).

Fig. 1.

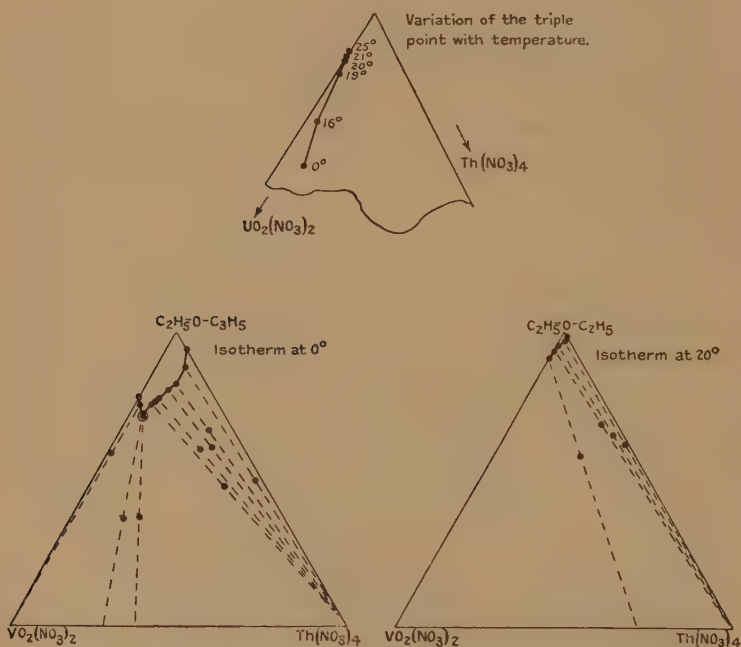


TABLE I. (Temperature 0°.)

$\text{UO}_2(\text{NO}_3)_2$.	$\text{Th}(\text{NO}_3)_4$.	Ether.	$\text{UO}_2(\text{NO}_3)_2$.	$\text{Th}(\text{NO}_3)_4$.	Ether.	Solid Phase.
22	0	78	—	—	—	$\text{UO}_2(\text{NO}_3)_2$.
22.5	1.02	76.48	40.1	0.52	59.38	$\text{UO}_2(\text{NO}_3)_2$
24	3.5	72.57	48.3	15.6	36.1	Both.
24	3.43	72.50	43	20	37	Both.
19.2	4.5	76.3	12	40	48	$\text{Th}(\text{NO}_3)_4$
18	5	77	—	—	—	"
16.5	5.6	77.9	13	27	60	"
12.2	7	81	9	30	61	"
8.2	8.3	82.5	7	26	67	"
3	8	89	1.8	48.5	39	"
0	5.8	94.2	—	—	—	"

TABLE II.

	$\text{UO}_2(\text{NO}_3)_2$.	$\text{Th}(\text{NO}_3)_4$.	Ether.	$\text{UO}_2(\text{NO}_3)_2$.	$\text{Th}(\text{NO}_3)_4$.	Ether.
0°	24	3.43	72.57	48.3	15.6	36.1
16°	17.7	1.7	80.6	28.2	20.4	51.4
19°	10.5	0.4	89.1	39.2	15	46.8
20°	8.78	—	91.22	15.5	26	58.5
22°	8	—	92	13.2	23	63.8
25°	7.37	—	92.63	12.2	30	57.8

It will be seen that the solubility in anhydrous ether of both salts, in presence of excess of both, falls markedly with the temperature, and that above 20° thorium nitrate is no longer soluble in a saturated solution of uranyl nitrate. At this temperature and above, the triple point falls on the side of the triangular diagram. Hence it follows that in order to secure a complete separation of uranium from thorium by means of anhydrous ether, the temperature must not be less than 20° and the uranium salt must be in sufficient excess to saturate the solution at that temperature.

Finally, it was thought useful to determine the isotherm for 20°. The results are shown in Table III. and also in the diagram (fig. 1).

TABLE III. (Temperature 20°.)

$\text{UO}_2(\text{NO}_3)_2$.	$\text{Th}(\text{NO}_3)_4$.	Ether.	$\text{UO}_2(\text{NO}_3)_2$.	$\text{Th}(\text{NO}_3)_4$.	Ether.	Solid Phase.
8.78	—	91.22	15.5	26	58.5	Both.
5.5	0.5	94	4.1	27	68.9	$\text{Th}(\text{NO}_3)_4$
3.1	1	95.9	2.1	32.2	65.7	„
—	1.4	98.6	—	—	—	„
—	1.6	98.4	—	—	—	„

It will be seen that at this temperature anhydrous thorium nitrate is soluble to the extent of 1.5 per cent. in anhydrous ether, and that the solubility diminishes to zero as the quantity of uranyl nitrate increases up to saturation, which is reached at 8.8 per cent.

Summary.

To throw light on the divergent results obtained in the use of ether for the analytical separation of uranium and thorium, the anhydrous ternary system—uranyl nitrate, thorium nitrate, ether—has been examined, and it has been shown that the conditions for the thorium not to be

dissolved are that the temperature must be above 20° and the uranyl salt sufficient to saturate the ethereal solution.

My thanks are due to Professor Soddy for suggesting the work, and to Professor Parravano for his advice in carrying it out.

University of Rome.

LXXX. *On the Thermal Expansions of Mercury and Vitreous Silica.* By F. J. HARLOW, B.Sc., A.R.C.Sc., F.Inst.P., D.I.C.*

Introduction.

THE importance in Thermometry of Precision of an accurate knowledge of the thermal expansion of mercury over as wide a range of temperature as possible is so well known that the appearance of a further publication on this subject embodying the most recent information calls for no excuse.

Since the publication by the author in 1914 (Proc. Phys. Soc. London, Feb. 1914) of the results of measurements of the thermal expansion of mercury contained in an envelope of vitreous silica, measurements of the absolute expansion of mercury for the range 0° to 100° C. have been made by Chappuis (*Trav. et Mém. Int. Bur. des Poids et Mes.* 1917), using the Callendar-Regnault method with several modifications introduced to eliminate certain errors which it was considered might be present in the determinations carried out by Callendar and Moss (Phil. Trans. A, vol. ccxi. Jan. 1911). The results obtained by Chappuis are in much closer agreement with the values published by the author and with Chappuis's values previously obtained by his weight thermometer of "verre dur" than are those obtained by Callendar and Moss, as reference to the values of the coefficients of expansion quoted in Table I. show.

Further, since 1914 additional observations have been made by several observers of the thermal expansion of vitreous silica which make it possible to deduce with greater precision the real expansion of mercury from the author's values of the apparent expansion. The final results, shown in column 5 of Table I., are in closer agreement with those of Chappuis than are those published by the author in 1914 and shown in column 3 of the same table.

* Communicated by the Author.

In the present paper the most probable values of the thermal expansion of both vitreous silica and mercury are considered over the range of temperature 0° to 300° C., and in each case the results are expressed in the form of suitable equations. In addition, tables are constructed from which the volume of 1 c.c. of mercury at 0° C. may be readily obtained at other temperatures throughout the range 0° to 300° C.

TABLE I.

Coefficients of Expansion of Mercury multiplied by 10⁸.

Temp. Range.	1. Chappuis' Wt. Therm., 1907.	2. Callendar & Moss's absolute method, 1911.	3. Harlow's Silica Wt. Therm., 1914.	4. Chappuis' absolute method, 1917.	5. Harlow's Silica Wt. Therm., present paper.
0-30°.....	18171	18095	18168	18189	18175
0-50°.....	18183	18124	18188	18206	18192
0-75°.....	18211	18163	18213	18227	18216
0-100° ...	18254	18205	18244	18248	18247

The Thermal Expansion of Vitreous Silica.

Range 0° to 100° C.

In the range 0° to 100° C. the available measurements of the thermal expansion of clear vitreous silica are as follows:—

- (a) Chappuis (*Procès-Verbeaux. Com. Inter. des Poids. et Mes.* 1903). Cylindrical specimen by comparison with a platinum-iridium tripod. Range 0° to 83° C.
Linear coefficient:

$$S_0^t \times 10^8 = 38.5 + 0.115 t.$$

- (b) Scheel (*Verh. d. Deutsch. Phys. Gesell.* v. 1903). Cylindrical specimen by comparison with a quartz crystal ring. Range 15° to 100° C.
Linear coefficient:

$$S_0^t \times 10^8 = 32.2 + 0.147 t.$$

- (c) Scheel (*Verh. d. Deutsch. Phys. Gesell.* ix. 1907). Ring specimens by absolute method. Range 0° to 100° C.

Linear coefficients :

$$(i.) S_0^t \times 10^8 = 21.7 + 0.2379 t.$$

$$(ii.) S_0^t \times 10^8 = 38.8 + 0.1682 t - 0.000504 t^2.$$

- (d) Donaldson (Proc. Phys. Soc. Lond. xxiv. 1912).
Metre rod by comparison with (i.) invar metre, (ii.)
nickel metre, (iii.) 43 per cent. nickel steel metre.
Range 0° to 30° C.

Mean equation for linear coefficient :

$$S_0^t \times 10^8 = 38 + 0.11 t.$$

- (e) Callendar and Eagle (see author's paper, *loc. cit.*
1914).

Linear coefficient :

$$S_0^t \times 10^8 = 78.0 - \frac{8650}{t + 175}.$$

- (f) Scheel and Heuse (*Verh. d. Deutsch. Phys. Gesell.*
xvi. 1914). Range 16° to 100° C.

Linear coefficient :

$$S_0^t \times 10^8 = 36.2 + 0.1813 t - 0.000340 t^2.$$

- (g) Souder and Hidnert (Scientific Papers, Bureau of
Standards, no. 529, vol. xxi. 1926). Rods of silica
30 cm. long.

Linear coefficient :

$$S_{20}^{60} \times 10^8 = 40. \quad S_{20}^{100} \times 10^8 = 45.$$

The values of the linear coefficient of expansion calculated from the above formulæ for ranges of temperature employed by the author in his experiments on the thermal expansion of mercury are shown in Table II. Souder and Hidnert's values were reduced to the ranges 0° to t° C. from their results for the ranges 20° to t° C. by plotting, assuming a linear variation with temperature of the coefficient between 0° and 100° C.

There is a very fair measure of agreement among the results obtained by the various authors, and it is considered that the average values given in the last column of Table II. can be applied with considerable precision to the author's measurements of the apparent expansion of mercury for the purpose of evaluating the real expansion.

TABLE II.
Linear Coefficients of Expansion of Silica multiplied by 10^3 .

Temperature Range.	1. Chappuis, 1903.	2. Scheel, 1903.	3. Scheel, 1907. (i.)	4. Scheel, 1907. (ii.)	5. Donaldson, 1912.	6. Callendar & Eagle, 1912.	7. Scheel & Heuse, 1914.	8. Souder & Hidnert, 1926.	Average Values.
0-30° C. ...	42.0	36.6	28.8	43.4	41.3	35.8	41.3	34.8	38.0
0-50° C. ...	44.3	39.6	33.6	45.9	43.5*	39.6	44.4	37.1	41.0
0-75° C. ...	47.1	43.2	39.5	48.6	46.4*	43.4	47.9	40.1	44.5
0-100° C. ...	50.0*	46.9	45.5	50.6	49.0*	46.6	50.9	43.0	47.8

* Extrapolated.

Range 100° to 300° C.

For temperatures above 100° C. the most reliable observations are the following :—

- (a) Randall (Phys. Rev. xxx. 1910). Randall carried out a series of measurements with a clear fused quartz ring over the range 16° to 1100° C., employing the Fizeau method *in vacuo*. The measurements appear to have been carried out with very great care. By means of the average value of the coefficient from 0° to 16° C., viz.

$$S_0^{16} = 37.1 \times 10^{-8},$$

obtained as in Table II. from the results of the observers named therein, Randall's results have been reduced to ranges extending from 0° C., yielding the following values :—

$$S_0^{80} = 41.4 \times 10^{-8},$$

$$S_0^{220} = 51.3 \times 10^{-8},$$

$$S_0^{300} = 53.5 \times 10^{-8}.$$

- (b) Callendar and Eagle in 1912 (see author's paper, *loc. cit.* 1914). The expansion of a fused silica rod was measured by an interference method, and the results for the linear expansion are represented by the formula :

$$S_0^t \times 10^8 = 78.0 - \frac{8650}{t + 175}.$$

- (c) Scheel (*Zeits. f. Physik*, v. 1921). Scheel, employing the Fizeau method, made measurements of the expansion of a fused quartz ring over the range 16° to 500° C. His results for the linear expansion are represented by the formula :

$$S_0^t \times 10^8 = 39.5 + 0.1282 t - 0.0001698 t^2.$$

- (d) Souder and Hidnert (*loc. cit.* 1926). These authors employed the comparator method and carried out observations with specimens 30 cm. long over wide ranges of temperature, which include observations for the range 20° to 300° C. Five different samples of transparent silica were used. Although the values obtained in different tests and with different specimens show rather large variations, yet it is considered that the final average result is entitled to some weight on

account of the large number of tests made and the use of five different transparent specimens. The final results for the linear coefficients of expansion for the ranges indicated are as follows :—

$$S_{20}^{100^{\circ}} \times 10^8 = 45, \quad S_{20}^{200^{\circ}} \times 10^8 = 48, \quad S_{20}^{300^{\circ}} \times 10^8 = 52.$$

These, when reduced to ranges from 0° C. by plotting, become

$$S_0^{100^{\circ}} \times 10^8 = 43, \quad S_0^{200^{\circ}} \times 10^8 = 47, \quad S_0^{300^{\circ}} \times 10^8 = 51.$$

A summary of the values of the coefficients of linear expansion of vitreous silica obtained in the above four researches, together with the final average values for the various ranges, are shown in Table III.

TABLE III.

Linear Coefficients of Expansion of Silica multiplied by 10^8 .

Temp. Range.	Randall, 1910.	Callendar & Eagle, 1912.	Scheel, 1921.	Souder & Hidnert, 1926.	Average Values.
0–100° C.	43.5	46.6	51.0	43.0	47.6*
0–200° C.	51.0	55.0	58.3	6.7	52.8
0–300° C.	53.5	59.8	62.7	50.9	56.7

* Average of all values, Tables II. and III.

The values for various temperatures over the range 0° to 300° C. of the average values of the linear coefficient of expansion are shown in fig. 1. These values are well represented within the limits of variation of the experimental results by the formula :

$$S_0^t \times 10^8 = 66.3 - \frac{3879}{t + 103}.$$

The coefficient of cubical expansion, taken as three times the linear coefficient for the reasons given in the author's earlier paper (*loc. cit.* 1914) are represented by the formula :

$$S_0^t \times 10^8 = 198.9 - \frac{11637}{t + 103}.$$

This type of formula is preferable to a cubic equation of the ordinary type, as it lends itself much more readily to the

calculation of the value for any particular temperature range.

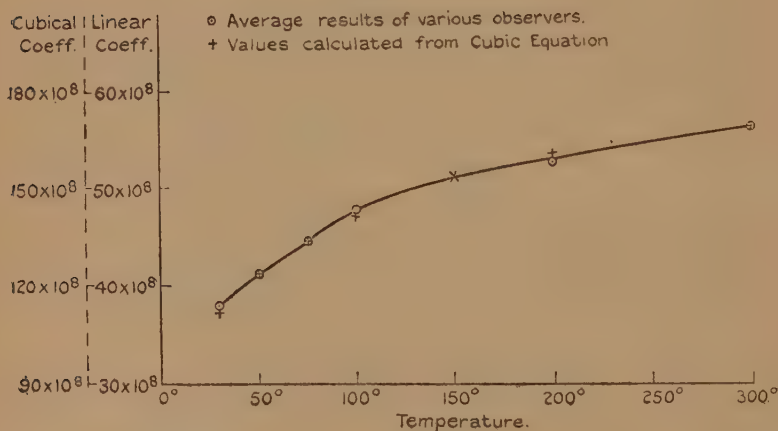
The following quartic equation which represents the variation in volume of an isotropic vitreous silica bulb over the range 0° to 300° C. may, however, be convenient for some purposes :—

$$\frac{V_t}{V_0} = 1 + 10^{-8} \{ 93.6t + 0.7776t^2 - 0.003315t^3 + 0.000005244t^4 \}$$

The Thermal Expansion of Mercury.

From the curve representing the cubical expansion of vitreous silica the quantities to be added to the author's

Fig. 1.



values of the apparent coefficient of expansion of mercury have been calculated, and are set out together with the derived values of the real coefficients of expansion of mercury in Table IV.

In Table V. are collected the results obtained by various observers for the real coefficient of expansion of mercury together with the values derived from various formulæ which have been selected to represent the results.

The close agreement at the lower temperatures between the results obtained under such widely different conditions as those quoted in columns 2, 3, and 4 justifies their acceptance as a very close approximation to the true values. These results were obtained with

- (a) The vitreous silica weight thermometer by the author (1914).
 (b) The weight thermometer of "verre dur" by Chappuis (1907).
 (c) The absolute method by Chappuis (1917).

They all differ somewhat from the results shown in column 1 of Callendar and Moss, obtained by the absolute method. For the higher ranges of temperature the agreement between the results obtained with the silica weight thermometer (column 2), and those of Callendar and Moss (column 1) is sufficiently close for their mean to be accepted as a close approximation to the true values.

TABLE IV.

Temp. range.	Volume Coeff. of Expansion of Vitreous Silica, $\times 10^6$.	$\frac{M+m}{M}$	$\frac{M+m}{M} \times S_0$ $\times 10^6$.	Apparent Coeff. of Expansion of Mercury, $\times 10^6$.	Real Coeff. of Expansion of Mercury, $\times 10^6$.
0-30° C.	114.0	1.005	115	18060	18175
0-50° C.	123.0	1.009	124	18068	18192
0-75° C.	133.5	1.014	135	18081	18216
0-100° C.	142.8	1.018	145	18102	18247
0-140° C.	150.9	1.024	155	18150	18305
0-184° C.	156.6	1.032	162	18220	18382
0-200° C.	158.4	1.035	164	18248	18412
0-250° C.	163.8	1.044	171	18356	18527
0-300° C.	170.1	1.052	179	18489	18668

*Representation of Thermal Expansion of Mercury
by Formulæ.*

In column 5 of Table V. are shown values of the coefficient of expansion which for the ranges 0° to 30° C. and 0° to 100° C. are the average values of those tabulated in columns 2, 3, 4. The values for the ranges 0° C. to 200° C. and 0° C. to 300° C. are the mean values of those tabulated in columns 1 and 2. The form of equation which represents best the experimental results for the variation in volume over the whole range of temperature from 0° to 300° C. is a quartic equation. The following quartic equation has been

TABLE V.

Temperature Range.	1. Callendar & Moss's absolute measurements, $\times 10^3$.	2. Harlow's Wt. Therin. of Vitreous Silica, $\times 10^3$.	3. Chappuis' Wt. Therin. of "verre dur," $\times 10^3$.	4. Chappuis' absolute measure- ments, $\times 10^3$.	5. Values used for deriv. of equations, $\times 10^3$.	6. Values calc. from Quartic (Harlow), $\times 10^3$.	7. Values calc. from Quartic (Sears), $\times 10^3$.	8. Values calc. from Cubic (Harlow), $\times 10^3$.
0-30° C.	18095	18175	18171	18189	18178	18178	18174	18170
0-50° C.	18124	18192	18183	18206	—	18196	18194	18192
0-75° C.	18163	18216	18211	18227	—	18221	18221	18219
0-100° C.	18205	18247	18254	18248	18250	18250	18251	18250
0-140° C.	18280	18305	—	—	—	18304	18306	18306
0-184° C.	18371	18382	—	—	—	18378	18379	18379
0-200° C.	18406	18412	—	—	18409	18409	18410	18409
0-250° C.	18525	18527	—	—	—	18522	18522	18520
0-300° C.	18557	18662	—	—	18663	18663	18663	18663

calculated by making use of the values of expansion coefficients shown in column 5:—

$$\frac{V_t}{V_0} = 1 + 10^{-8} \{ 18153.8 t + 0.7548 t^2 + 0.001533 t^3 + 0.00000536 t^4 \}.$$

The values of the expansion coefficients calculated from this equation for the various ranges employed in the author's experiments are given in column 6. Their close agreement with the values obtained experimentally as set out in column 2 will be observed.

In the discussion of the author's earlier paper, Mr. Sears, of the National Physical Laboratory, gave the following quartic equation, which he derived on certain assumptions from the experimental results then available, viz.:—

$$\frac{V_t}{V_0} = 1 + 10^{-8} \{ 18145.6 t + 0.9205 t^2 + 0.0006608 t^3 + 0.000006732 t^4 \}.$$

The values of the expansion coefficients calculated from this equation are given in column 7 of Table V. It will be seen that a very close agreement exists between the values obtained from the two quartic equations, so that the present investigation may be taken as a verification of the accuracy of the quartic equation given by Sears, full particulars of the derivation of which were published in the discussion on the author's paper of February 1914 (*loc. cit.*).

In order to furnish in the present paper a table of values of the volume of 1 c.c. of mercury at 0° C. when measured at various temperatures over the range 0° to 300° C., it was found to be much more convenient to employ an equation of the type

$$\frac{V_t}{V_0} = 1 + \left(a + \frac{b}{c-t} \right) t \times 10^{-8}.$$

The following values of the constants were calculated from the coefficients of expansion shown in column 5 of Table VI. for the ranges 0° to 100° C., 0° to 200° C., 0° to 300° C., viz.:—

$$a = 17559.1,$$

$$b = 369555,$$

$$c = 634.7.$$

The equation containing these constants represents the experimental results with considerable accuracy well within the limits of variation of the experimental results shown in columns 2, 3, and 4, particularly for the range of temperature

100° to 300° C. In column 8 of Table V. are shown the values of the expansion coefficients calculated by means of the corresponding equation, viz. :—

$$\alpha_0^t \times 10^8 = 17559 \cdot 1 + \frac{369555}{634 \cdot 7 - t}.$$

Table of Volumes and Expansion Coefficients.

Table VI. gives the values of the expansion coefficient calculated for the temperature ranges 0° to 10°, 0° to 20°, 0° to 30°, etc., up to 0° to 300° C. It also gives in a manner leading to easy interpolation the volumes occupied by 1 c.c. of mercury at 0° C. when measured at various temperatures in the range 0° to 300° C. The application of the usual proportionate interpolation gives results well within the limits of accuracy of the experimental determinations.

In the compilation of Table VI use was made of the quartic equation for the range 0° to 100° C. and of the cubic equation for the higher ranges up to 300° C., as follows :—

Range 0° to 100° C.

$$\frac{V_t}{V_0} = 1 + 10^{-8} \{ 18153 \cdot 8 t + 0 \cdot 7548 t^2 + 0 \cdot 001533 t^3 + 0 \cdot 00000536 t^4 \}.$$

Range 100° to 300° C.

$$\frac{V_t}{V_0} = 1 + \left\{ 17559 \cdot 1 + \frac{369555}{634 \cdot 7 - t} \right\} t \times 10^{-8}.$$

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LXXXI. *The Application of a Valve Amplifier to the Measurement of X-Ray and Photoelectric Effects.* By J. BRENTANO, D.Sc., Lecturer in Physics, Manchester University*.

MY attention has been directed to a paper by Mr. Wynn-Williams with the above title in the August number of the Philosophical Magazine†.

I was particularly interested in Mr. Wynn-Williams's results, as the arrangement adopted by him bears close resemblance to an arrangement for measuring ionization

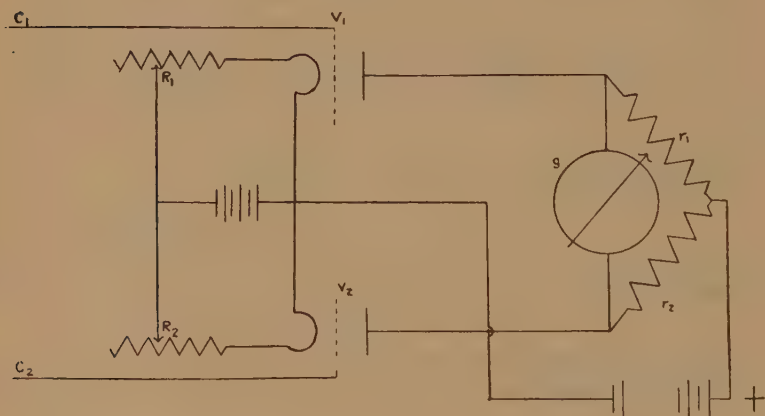
* Communicated by the Author.

† C. E. Wynn-Williams, Phil. Mag. vi. p. 324 (1928).

currents described by me in 'Nature,' Dec. 22nd, 1921. This was introduced as a more sensitive method to take the place of the method evolved by Malassez for the measurement of X-ray intensities, where greater sensitivity is required, and was demonstrated by some experiments showing the change of ionization along the path of α -rays (Bragg's curves) *.

Mr. Wynn-Williams does not quote the earlier publication in his present paper, and it will indeed have escaped the attention of most readers, so that it may be recalled with a few words. In order to shorten the discussion, the diagrammatic sketch given in 'Nature' may be referred to again (see fig. 1).

Fig. 1.



The three electrode valves V_1 and V_2 form two arms of a Wheatstone-bridge containing the galvanometer g , the two other arms of which consist of ohmic resistances r_1 and r_2 ; a common high-tension battery is used for the anode currents of the two valves, and a common battery is also used for supplying the heating currents to the filaments, which are

* J. Brentano, 'Nature,' cviii. p. 532 (1921).

The comments I wish to make refer to the general method, as the various applications depend on the sensitivity, steadiness, and immunity from external disturbances of the bridge method used. In connexion with my own work I was particularly interested in X-ray measurements when discussing the arrangement in 'Nature.' For the development of a valve amplifier and the study of the particular conditions of photoelectric measurements the work of Meyer, Rosenberg and Tank, *Arch. Sc. Phys. et Nat.* (5) p. 260 (1920) and of Rosenberg, *Zeitschr. f. Phys.* vii. p. 18 (1921) should be considered, which seem not to have been noticed by Mr. Wynn-Williams.

controlled by resistances R_1 and R_2 . Any variation of the potential of the grid of one of the valves produces a deflexion of the galvanometer. The purpose of the second valve is to introduce in the two adjacent arms of the bridge elements which can be adjusted so as to present similar characteristics with respect to any variation of the E.M.F.'s acting in the circuit.

It will be seen that this arrangement is practically the same as the arrangement used by Wynn-Williams, except that he controls the ratio of the heating currents of the two filaments by interposing a slide-wire resistance of constant value and a sliding contact instead of the two separate resistances R_1 and R_2 . He also acknowledges this similarity in a previous publication, to which reference is made in his present paper, where he describes the arrangement discussed in 'Nature' in general terms, and refers to it as the "old method," emphasizing that the modification introduced by him consists in the slide-wire, which, in conjunction with the discussion given in the paper, is considered to be an improvement of vital importance*.

Comparing the limit of sensitivity obtained by Wynn-Williams, which for current is 10^{-12} – 10^{-13} amp. and for voltage $1.6 \cdot 10^{-4}$ volt, with the sensitivity found in my early experiments with valves and instruments not particularly suitable for obtaining the best results, which was $3 \cdot 10^{-13}$ amp. resp. $1.2 \cdot 10^{-4}$ volt, the improvement introduced by the slide-wire is not apparent, and it seems, indeed, mainly a question of the technical execution whether there is a preference for one or the other way, so that I find it difficult to agree with him on this particular point.

The limits of the sensitivity obtained by Wynn-Williams are actually imposed by the unsteadiness of the arrangement, and the discussion given in his paper shows that some points have not been considered which are essential for the practical operation of the method and which lead to an application which in some respects may appear more efficient. Although desiring to appreciate his work, some criticisms cannot be

* C. E. Wynn-Williams, Proc. Camb. Phil. Soc. xxiii, p. 811 (1927). Cp. fig. 1 b and fig. 1 c with the figure reproduced from 'Nature.' In discussing the merits of the alteration, it is said (p. 814): "The necessary modification seems at first sight to be so superficial as to render such a claim absurd, it consisting merely of 30 cm. of eureka wire. . . . But a consideration of the theoretical side of the question shows that this is not the case, the inclusion of the slide-wire EF being the most natural and simplest way of enabling certain theoretical conditions to be realized experimentally, and not a haphazard addition to an existing older circuit."

omitted in order to do full justice to the bridge method employed.

In the discussion Wynn-Williams considers a particular way of operation which neglects some of the possibilities for compensating the effect of the inequality of the two valves with respect to variations of the E.M.F.'s acting in the circuits, and which takes no account of the particular features of the modern highly-evacuated valves. Applying the relation of the Wheatstone bridge, the effect of voltage fluctuations in the two battery circuits is considered, giving particular attention to the compensation of fluctuations in the heating circuit*. In doing this he finds it difficult to obtain at the same time compensation of variations in the anode circuit, and no practical way is indicated for carrying this out independently, so that it is suggested to disregard compensation for the latter.

This is probably the reason why, in the earlier experiments of Wynn-Williams, without special shielding external perturbances were greatly felt, so as to induce him to recommend the instrument as a sensitive wireless detector.

Another reason which may contribute to unsteadiness is possibly due to the fact that while connecting one grid to the collecting electrode of the ionization chamber and keeping the other grid insulated, no consideration seems to be given to the capacity connected to each grid. When using the method in this particular way, an essential condition for obtaining steadiness is that the capacities connected with the grids should be of the same order, the exact values depending on the characteristics of the two valves and on the insulation of each grid.

In his recent experiments Wynn-Williams is successful in operating the instrument in the neighbourhood of an X-ray bulb. This is obtained by very careful screening, and can thus scarcely be considered as a test for the intrinsic merits of the method. In fact, it has been shown by Du Prel † that X-ray measurements can be carried out with a valve arrangement with a very high degree of sensitivity, which has no compensating features, when proper shielding precautions are taken.

The point which merits special attention refers to the particular properties of the highly-evacuated valves which are now available. In my early experiments described in

* A. Marcus, *Phys. Rev.* xxxi. p. 302 (1928), gives prominence to the same point.

† Du Prel, *Ann. d. Phys.* lxx. p. 199 (1923).

'Nature,' only soft valves were available so that it was impossible to establish a sufficiently dense space-charge in the neighbourhood of the filament. In such conditions the anode current varies greatly with any change in the temperature of the filament, and the control of the heating current is therefore of the greatest importance. Mr. Wynn-Williams concentrates his attention on the same point, whereas the fluctuations of the heating current with highly-evacuated valves have actually comparatively little effect when the valves are used under suitable conditions. It will also be found possible to dispose the heating circuit in such a way as to greatly reduce the effect of electromagnetic disturbances while the anode circuit containing the bridge is much more exposed, and compensation with respect to variations of the E.M.F. acting in this circuit should therefore be considered in the first place. This compensation was only alluded to in my note and has been discussed in a paper read at the Hambourg meeting of the Physical Society last summer.

The main points of the method may be summarized :—

The heating currents of the valves, which are of the low-temperature emitting type and highly evacuated, have such values that the filaments are surrounded by sufficiently dense space-charges.

Referring to the well-known equation :

$$i_a = aV_g + bV_a + c,$$

which may be used to indicate for the purpose of the discussion in approximation the relation between the anode current i_a , the grid voltage V_g , and the anode voltage V_a , the quantities a , b , and c being constants; by differentiating

$$b = \frac{\partial i_a}{\partial V_a}.$$

It will thus be seen that in order to establish

balance in the bridge and to maintain this for a variation of the E.M.F. in the anode circuit, the double relation

$$i_1 : i_2 = r_2 : r_1$$

and
$$b_1 : b_2 = r_2 : r_1$$

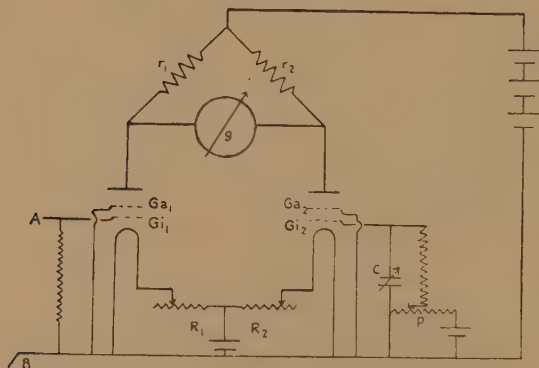
must be satisfied, where the indices 1 and 2 refer to the two valves of the bridge. From the second equation a definite ratio is therefore fixed for the resistances r_1 and r_2 , and the equilibrium of the bridge has to be determined by giving proper values to the potentials of the grids. If the grid which is used for the measurement of potential differences or which is connected to the ionization chamber is given the

potential which corresponds to the state of equilibrium, a definite voltage must be applied to the grid of the other valve by connecting it to a potentiometer with a suitable E.M.F.

In this way a remarkable degree of immunity from external disturbances can be obtained. In one experiment, using purposely two valves of different type with greatly different characteristics for which the ratio $r_1/r_2=1.75$ was found to give correct balance, a change of the anode voltage by ± 2 volts produced a deflexion of the galvanometer of 0.3 scale-division; the sensitivity in this particular case was $2 \cdot 10^{-11}$ amp./scale-div.

When a high degree of sensitivity is desired, the electrostatic induction between the anode and grid of the valves

Fig. 2.



must be considered. Any variation of the potential of one of the grids is accompanied by a variation of the potential distribution of the anodes, which reacts on the grids; with a grid which is highly insulated or connected to earth through a high resistance a disturbance is thus produced. This effect can be reduced by reducing the resistances r_1 and r_2 (there is, in fact, no advantage when they are much larger than the resistance of the galvanometer), or more effectively by using valves with two grids, the outer grids being connected to earth. The current sensitivity observed with such an arrangement was $4 \cdot 10^{-14}$ amp., the voltage sensitivity $2 \cdot 10^{-5}$ volt, and the power dissipation for one scale-deflexion $8 \cdot 10^{-19}$ watt.

The arrangement which corresponds to these conditions is indicated by fig. 2. G_{a1} and G_{a2} are the outer grids, G_1

is the inner grid connected to A which can be brought in connexion with the ionization chamber while B leads to earth, G_{12} is the inner grid connected to the potentiometer p through a high resistance with a capacity c in parallel, in order to compensate for the capacity effect produced by external fields, which has been mentioned in the earlier part of this note.

The heating circuit was arranged so as to be compact and to present a minimum of "inductive area," and in operation no compensation of the heating circuit was found necessary, but this could easily be effected without interfering with the other compensating conditions if required. The use of double-grid valves is indicated here, as it increases the steadiness of the bridge, but actually the same sensitivity for current and for voltage was found with single grid valves, when the balancing conditions were observed.

It may be mentioned that the necessary variability so as to satisfy the relations imposed by the valve characteristics and to maintain the balance of the bridge with respect to fluctuations of the E.M.F.'s acting in the anode circuit can be obtained by interposing a resistance between one of the anodes and the galvanometer branch. In this way the potentiometer can be dispensed with; the setting is not quite so convenient.

Clarens,
Dec. 28th, 1928.

LXXXII. *On some Regularities in the Table of Elements, and their Cosmological Import.* By D. STRÖMHOLM *.

MENDELEJEFF arranged his system of the elements according to their atomic weight, assuming the qualities of the elements to be periodic functions of their atomic weight. This idea proved to work rather well, though there appeared to be a few exceptions, which caused much trouble. Now the state of these matters is totally altered; the elements are arranged according to the atomic numbers, which are found by means of the Röntgen spectra. The atomic number is considered to be determined by the number of electrons in the envelope of the atom; this is determined by the positive charge of the atomic nucleus,

* Communicated by the Author.

which is the excess of positive units over negative ones (electrons) in the nucleus. As the nuclei to a certain number of positive units can contain a varying number of electrons, it follows that one and the same atomic number can belong to different atoms of different atomic weights, but still of identical chemical properties, so called isotopes, the connexion between which is that the difference between positive and negative units in the nuclei is the same. That Mendelejeff's system is not quite exact therefore no longer causes any wonder. But it may be worth while to give some thought to the converse problem of how it is possible that Mendelejeff's system can be applicable to the extent that it actually is. Its approximate validity shows, of course, that the atomic weight of an element, respective the mean value of the atomic weights of its isotopes, is connected with the atomic numbers by some fairly strict rules.

The cause of the existence of isotopes being that in the atomic nuclei, together with the positive units of weight 2, there can exist negative units, electrons (of an all but infinitesimal weight), our task is to investigate if the percentage of the electrons in the nuclei is dependent on the atomic weight. For the rest, the common conception seems to be that the positive units themselves contain electrons; thus that they are composed of two positive units of weight 1, cemented together by one electron; but we do not propose to deal with such electrons here. If there existed no electrons in the nuclei, then the atomic number would be equal to half the atomic weight, the weight of a positive unit being 2. Such is, indeed, the case in many elements of a low atomic number up to No. 20 Ca, but in no higher element, and our investigation has thus only to consider the elements of high numbers, beginning with No. 21. Regarding these elements, we form a function for each of them denoting the proportion between positive and negative units in the nucleus. Half the atomic weight is equal to the number of positive units; the difference between this number and the atomic number gives the number of electrons in the nucleus; the quotient

between these two quantities, $\frac{\text{at. w.}}{2} : \left(\frac{\text{at. wt.}}{2} - \text{No.} \right)$, gives

the proportion between positive and negative units in the nucleus. It is this function that we shall use in the following, indicated posit./negat. We shall first give some examples of the values of posit./negat. No. 21, Sc 14.5; 30, Zn 12.1; 33, As 8.3; 47, Ag 7.7; 51, Sb 6.1; 92, U 4.4. If we write down all these values of posit./negat. in a row according to

the atomic numbers, we find the following rules:—Firstly, a certain steadiness in the progress of the row, the very cause of the validity of Mendelejeff's system; further, we find, as the cited examples show, that the values of posit./negat. decrease with the increasing atomic weights, *i. e.*, the higher the atomic weight the higher the percentage of electrons in the nuclei. Lastly, one more peculiarity appears, namely that this decline of the values posit./negat. is not gradual, but proceeds by distinctly pronounced leaps, separated by long stretches where the values are constant. From this point of view the table of the elements can thus be divided into distinct stages; these we shall treat separately. These stages are furthermore given yet more prominence by a special circumstance, that the first element of each stage is remarkably rare.

In the first stage, containing the elements up to No. 20, there exist, as said before, many elements the atomic number of which is equal to half the atomic weight, and which have therefore no electrons in the nuclei. Still another circumstance, found in the investigation of isotopes, is to be mentioned here: if the weight of all positive units were 2, it would result that the atomic weight of all isotopes would be expressed by even numbers; but as many isotopes are known the atomic weight of which is an odd number, there must also exist positive units of an odd weight, certainly 3. As a matter of fact, most cases among elements belonging to the first stage, where the atomic number is less than half the atomic weight, seem to depend on the occurrence of positive units of the weight 3. I think, therefore, that if we say that the ratio posit./negat. in this stage is infinitely great, we express the essential matter, though the rule suffers exceptions.

The second stage comprises Nos. 21–30, from the rare Sc to Zn. The values posit./negat. are: No. 21—Sc 14·5; Ti 12·3; V 10·2; Cr 13·0; Mn 11·2; Fe 14·7; Co 11·8; Ni 21·7; Cu 11·4. No. 30—Zn 12·1. The average of the whole stage is 13·3; of Nos. 21–25 it is 12·2; of Nos. 26–30 it is 14·3 (or, if Ni is excluded, 12·5). Though the values vary rather much, they show thus no tendency at all to decrease at the higher atomic weights, which still holds good if we exclude the very irregular Ni. The stage is thus well marked.

The third stage comprises Nos. 31–47, from the rare Ga and Ge at least to Ag. The values of posit./negat. are: No. 31—Ga 9·0; Ge 8·5; As 8·3; Se 7·1; Br 8·1; Kr 7·6; Rb 7·4; Sr 7·5; Y 8·1; Zr 8·1; Nb 8·1; Mo 8·0; Ru 7·4;

Rh 7·9 ; Pd 7·2. No. 47—Ag 7·7. The average for the whole stage is 7·8 ; for 31–38 it is 7·9 ; for 39–47 it is 7·8. The stage is thus well marked.

The borders on the next stage are somewhat confused, Nos. 48 and 49 both showing the intermediate value 6·9. As 49 In is very rare, it is probably the first element of stage 4. The range of atomic weights over which the second stage extends may be expressed by the difference in atomic weight between Ca, the last element of stage 1, and Zn, the last one of stage 2, and is thus about 26. The range of stage 3, a little vague, as we have seen, is about 45 ; thus much greater than that of stage 2. It seems thus that a higher stage has a greater range than a lower one ; true, the range of the first stage is greater than that of the second, but it is very possible that the first stage is equivalent to more than one of the following stages, a subject that we shall return to later on. The discerning of stages in the highest part of the system is not so sure. The average of posit./negat. of Nos. 50–60 is 5·85, with the extremes 6·3 and 5·4 ; of Nos. 62–72 it is 5·4 ; of Nos. 73–83 it is 5·0, with the extremes 5·1 and 4·9. Probably two stages, the fourth and the fifth, are to be discerned, the boundary between which lies somewhere among the rare Nos. 61–72. If we apply the rule that the ranges of the stages increase towards the higher part of the system, we ought to place the border as high as possible : thus at 72 Hf the two most stable elements from the radioactive part of the system, Th and U, have both the low ratio posit./negat. = 4·4 ; but as these values do not belong to the average of many isotopes, but to single isotopes, which are preserved by the slowness of their radioactive disaggregation, they are not comparable to the other values, and cannot be sufficient to assign the radioactive elements to a stage of their own. Indeed, if stage 5 commences with 72 Hf, then its range may extend beyond the highest known radioactive elements. For the different stages we have thus found the following averages of the values posit./negat. :—Stage 1 = ∞ ; st. 2 = 13·3 ; st. 3 = 7·8 ; st. 4 = 5·85 ; st. 5 = 5·0.

The figures on which the mentioned regularities are founded are, of course, not altogether unobjectionable. Some atomic weights are the average of isotopes, whilst other elements are homogeneous, and it may seem questionable if they are altogether comparable ; from Aston's table of isotopes, however, it is evident that in the former cases, as a rule, the weights of the most important isotopes are not very different. The occurrence of isotopes of an odd atomic weight, thus of positive units of weight 3, is certainly a

cause of errors. In such cases the atomic weight ought, of course, to be corrected so that the unit 3 was reckoned only to weigh 2; the atomic weight would be diminished by 1. As Aston's table of isotopes is complete up to No. 40, such a correction can be made up to this number; and it is thus easy to verify that the rules stated are not impaired hereby. It might be maintained that it were possible that two units of weight 3 would occur in one atom, which could not be perceived, as the atomic weight would then be even, but would affect our results appreciably. But in the first stage this is impossible in most cases, in consequence of the smallness of the atomic weights. It is moreover obvious that, if there can be discerned any general rule about the occurrence of the units 3, this would prove that their occurrence is ever manifest, never disguised. As a matter of fact, such a rule is to be discerned in Aston's table as valid over the whole range of elements (except the very lowest up to No. 7); the isotopes of an odd atomic weight occur well-nigh exclusively in elements of an odd number, and these are well-nigh exclusively composed of such isotopes.

In consequence of this rule, the corrections mentioned for the occurrence of the units of weight 3 have the effect that the values posit./negat. are raised in all elements of odd numbers, not in the even ones. Regarding stage 2, this amendment renders the values more equable, except that of Sc, which becomes rather high. In the higher stages, however, the uncorrected values are already rather higher in the odd than in the even elements, which circumstance then becomes enhanced by the correction. It seems, then, as if the occurrence of the units 3 would lessen the capacity of the nuclei to absorb electrons: this may seem intelligible, as these units of weight 3 certainly are bigger than the ordinary ones, and therefore encroach upon the room available.

Regarding the lowest stages, it may be of interest to note the absolute number of electrons too. In stage 2, where many of the elements are homogeneous, the nuclei contain mostly two electrons. Only in the highest elements, Cu and Zn, do isotopes with three electrons attain some importance. But, in addition, nuclei with one electron occur in this stage rather irregularly, namely in Sc, in the chief isotope of Ni, and in a subordinate one of Fe. The isotopes of stage 1, which have electrons in the nuclei, contain as a rule one, argon two. The unsteadiness of the values posit. negat. in stage 2 depends partly on so many elements being homogeneous, but most on the irregular occurrence of atoms with one electron.

The rules that we consider here are thus :—(1) The percentage of electrons in the nuclei is zero in the elements of low atomic weights ; it commences to be evident at No. 21, and increases then with increasing atomic weights : (2) this increase is not gradual, but proceeds in distinctly marked stages.

These rules seem apt to give occasion to theoretical speculations, and the basis of these can only be hypotheses about the genesis of the elements, at least the heavier ones. Such a notion has been rendered somewhat familiar by the discovery of the radioactive transmutations, which show that the elements are not essentially unalterable. At least the radioactive elements, being perishable, must have been created ; true, the fundamental elements, U and Th, have very long periods, and by assuming great original stores of them, the commencement of things would be placed at a distance, though not infinitely, at least excessively great ; but as the stable ultimate products of the radioactive reactions exist only in insignificant quantities, such an assumption is not admissible. The radioactive reactions of disintegration proceed under an extremely great development of energy ; the radioactive elements are thus strongly endothermical. It is then a rather necessary conclusion by analogy that the elements of high atomic weights are altogether endothermical, though it is uncertain how far down in the series this holds good. The only locality where the creation of elements can be supposed to take place is the interior of the earth and other celestial bodies ; the huge concentration of energy by heat and pressure that must be assumed to prevail there makes it acceptable as the birth-place of formations very rich in energy.

That most elements seem to be totally unalterable is no essential hindrance, as it is very common that reactions which do not take place at lower temperatures come to pass at higher ones. The radioactive reactions, however, though showing that the elements are not essentially unalterable, have given a hard check to speculation ; the speed of these reactions has proved to be independent of the temperature, which is totally different from the laws of ordinary chemical reactions, and seems to make it dubious if experience from the latter is to be applied at all to element-shaping reactions. But still it seems inadmissible to assume an altogether essential difference between these two classes of reactions, and it does not seem impossible to guess in which direction an explanation of the puzzling insensibility of element-reactions to temperature is to be sought for. Other

paradoxes from the province of the science of heat are known which are explained thus: that the expected exchange of energy is prevented, by some cause or other, from being realized; for instance, in the Leiden frost phenomena it is the question of a screen of gases. Now the atoms are supposed to consist of a nucleus, the seat of the radioactive reactions, surrounded by a swarm of electrons; it may be this, principally its outermost layer, that prevents the energy from without from attaining to the nucleus. But in the interior of the earth, not only may the temperature be very high, but the electron envelope is exposed to an enormous pressure which prevents its movements, and thus prevents it from appropriating the energy, which then may penetrate to the nucleus. It seems admissible to assume that in the interior of the earth element-shaping reactions take place, though probably slowly, certainly resulting in equilibria the components of which are elements.

The main features of the conditions of these equilibria ought to be as follows:—The effect of high temperature is that endothermic elements are favoured, according to our assumption elements of high atomic weight. The pressure tends to diminish the volume. As the volume mainly depends on the electron envelope, this is compressed in the first place; but to this it opposes an extraordinary resistance; therefore also element-reactions, diminishing the volume, may attain importance. Such an one is certainly the increase of the atomic weights; thus the collection of matter in greater heaps. Ordinarily the specific gravity is great when the atomic weight is high; and by comparison of homologous elements we find, indeed, the specific gravity regularly increasing with the atomic weight. We find it thus probable that high temperature and high pressure work in the same direction, increasing the atomic weights. Further, as it is mainly the electron envelope that determines the volume, the removal of electrons must cause reduction of the volume, and thus be an effect of pressure; such a removal is effected by the absorption of electrons into the nuclei. We have seen, indeed, that the greater the atomic weight is, the greater is the percentage of electrons in the nuclei; it is therefore logical to assume that it is one and the same cause that makes the mass of the nucleus and its percentage of electrons increase. This common cause is the pressure that prevailed in the *milieu* where the element was created.

The percentage of electrons in the nuclei would thus give us a direct measure of the pressure prevailing at the place where the element arose. The first elements up to No. 20

would therefore not require a very high pressure for their creation, whilst this is the case in all elements of higher numbers, the higher the atomic weight the greater must the pressure be, and the greater therefore is the depth from which the element came. Furthermore, we have found that the increase of the percentage of electrons with the atomic weight is not gradual, but proceeds by leaps and is divided in several stages. This circumstance is, from our standpoint, only to be explained thus: that the interior of the earth, the birthplace of these elements, is not one homogeneous space where all transitions between elements are gradual and continuous, but is composed of several layers, each of them being a homogeneous space where all elements that belong to one of the stages mentioned above are created; elements of higher or lower atomic weights are perhaps not altogether missing, but very disfavoured in the existing equilibrium. Within such a layer comes a new one with a new, limited set of elements, and so on.

A thermodynamic explanation may be given to this conception. We know that the separation of positive units (as α -particles) from radioactive elements is a strongly exothermic process: then the inverse reaction must be endothermic, and we assume something of the kind to be valid in a great part of the element system. If we could build up the elements by affixing one positive unit after the other, we should then find these synthetic reactions endothermic, and this would hold good, at least from No. 21. But the heat absorbed would not in all cases have such, we may say, fantastic measures as are shown in the radioactive reactions; it is probably low in the lower parts of the element system, and increases with increasing atomic weights. This increase is not gradual, but proceeds by bounds: the quantity of heat absorbed at the affixing of one positive unit remains tolerably constant over a certain range; then it suddenly rises to a higher, probably a much higher, value, which then remains fairly constant over a new range, and so on. The elements which belong to such a range constitute a certain stage in our table of the ratios posit./negat. and also a layer in the interior of the earth. All this makes finally a certain conception of the structure of the nuclei rather probable, namely that they are composed so that one layer of positive units is heaped outside the others, each such layer corresponding to one stage in our table of the ratios posit./negat., except that the first stage perhaps corresponds to several layers. In such a structure each succeeding layer ought, of course, to be greater than that next within, and more so as the interior

in a new stage swells by the absorption of more electrons, and we have seen indications that each succeeding stage comprises a greater range of atomic weights than that preceding it.

Of these layers, corresponding to the stages of our table, the surface-layer comprises the elements of low atomic weights up to Ca, and these elements are therefore prevalent at the surface. Element-reactions may perhaps occur in the lower parts of this layer, or did so when the surface of the earth was hot; but the pressure is not sufficient to cause the absorption of electrons in the nuclei. Those isotopes where we have to assume that electrons occur in the nuclei may come from the innermost parts of this layer, or else, as for instance in the main isotopes of argon, we may assume that atomic weights, ordinarily belonging to this layer, can still exist to some insignificant concentration in the next layer. The latter, the first deep layer, consists of metals, among which iron probably is prevalent. The composition of the other deep layers is, in consequence of their greater range of atomic weights, not so monotonous as that of the iron layer; beside heavy metals there occur light metals and metalloids. Regarding the radioactive elements, there is sometimes, to determinations of their quantity, the remark added, that if their percentage is as great in the whole mass of the earth as at the surface, the development of heat at their decomposition would more than outweigh the radiation of heat of the earth, which then would become ever hotter. According to our assumption, there would exist in the innermost part of the earth great quantities of elements which would be radioactive if they were transported to the surface, but at their original home in the interior they are components of equilibria, and thus stable, not radioactive. If elements migrate from the interior upwards, which would give rise to exothermic reactions, this is certainly counter-balanced by migrations in the converse direction and of a converse effect.

Whilst the elements of the first stage are originally at home at the surface, all others come there by migration, and those from the deepest layers must pass, intermediately, layers in which they are not stable. We must then assume that the speed of the reactions, by which they are decomposed, is small in comparison with that of their wandering. In the iron layer, for instance, there is a continual immigration of elements from below, which then are continually decomposed, and the percentage of elements from deeper layers thus established is so great that considerable masses of them have passed to the surface. Probably many

quantitatively unimportant isotopes are intermediate products of decomposition, not coming from the proper layer of the element, but decomposed further so slowly that a little has been able to pass on to the surface. If the speed of wandering somewhere were much less for a certain element than it is as a rule, then this element would arrive at the surface only in a small quantity, far from corresponding to its frequency in its own layer. The wanderings of the elements may be occasioned, at least partly, by diffusion movements; therefore the speed of wandering would decrease if the element became a component of a chemical compound of a high molecular weight, and some cases where elements of similar chemical properties are rare might be explained in that way. We find two homologous elements, the manganese homologues 43 and 75, extremely rare. Each of them is followed by three elements, 44-46 and 76-78, the six platinum metals, chemically closely allied and all rather rare. No. 61 is not known and the row 62-71 consists of rare elements, all very similar to each other.

Another instance of remarkable rareness in elements we have already observed, the first element of each of the stages that we have discerned is rare, and there are indeed, at the commencement of each stage, some atomic weights missing or rare, which caused gaps in the range of the atomic weights. This is probably due to the great thermodynamic discontinuity that we assumed to divide each stage from the preceding one. The second stage commences with Sc, which is very rare for an element of so low an atomic weight; stage 3 commences with the excessively rare Ga and Ge; stage 4 probably with the very rare In; at the commencement of stage 5 there are several elements between which to choose, the most probable being Hf. That several of these introductory elements are trivalent seems only possible to be taken as a mere chance.

Still another circumstance may be mentioned here. The layers which we have assumed to be in the interior of the earth are certainly so thick that the pressure is considerably greater at their lower than at their upper border. Then in some elements different isotopes may be created in different parts in the layer, though they become well mixed afterwards through diffusion. In the second stage the percentage of electrons in the nuclei was exceptionally low in some cases, namely in Sc (corrected value) and in the chief isotope of Ni. These atoms originate probably in the uppermost part of the iron layer. Regarding Sc, which commences a stage and must be disfavoured in the equilibrium, it may be that

it can only be created in this part of the layer. Regarding Ni, it may be the mixing of the isotopes that has been imperfect, in consequence of an unusually small speed of wandering.

Other cases of rareness are probably due to instability; and as this is thought to depend on the nucleus, it might seem *a priori* that no connexion with the position in the system, which is determined by the envelope, could exist. Such seems, however, to be the case at least in one instance. All isotopes of the helium gas ^{86}Em are excessively short-lived, and the rareness of its lower homologues may be put in connexion with this.

Here we may think of the remarkable rule, mentioned above, that isotopes of an odd atomic weight, thus positive units of weight 3, are mainly connected with elements of odd numbers. The import of the odd numbers cannot be found in the nucleus, and must therefore be sought for in the envelope. True, in the first stage the nuclei of elements of odd numbers contain as a rule an odd number of positive units; but this is not the rule in the higher parts of the system. But in the envelope every element of an odd number has an odd number of electrons. In order to comprehend that this can have an influence on the components of the nucleus, it seems altogether necessary to assume that the electrons in the envelope join in couples, or at least that their movements are connected by pairs, so that in all odd elements, but not in the even ones, an uncoupled electron would occur: without this hypothesis any real effect of the contrast odd-even cannot be imagined. That a satisfactory theory of the atom must assume a tendency of the electrons in the envelope to combine by pairs I have emphasized some years ago*. It was there the question of the outermost layer of the envelope, the valency electrons. When a metalloid gives several compounds with negative elements, as for instance chlorine, the valency stages of the divers compounds differ by two, and it was then assumed that here all electrons are joined in pairs, also, by polymerization, the odd one in elements of odd numbers; in metals the valency electrons are free. The contrast odd-even just remarked makes it necessary to assume that under the conditions of pressure and heat prevailing in the interior of the earth this tendency to join in couples is universal; the layer of the valency electrons has not any other character than the other parts of the envelope, and the difference between metals and metalloids is effaced. On the other hand, any coupling of electrons

* *Zeitschrift für anorgan. und allgem. Chemie*, cxi. p. 237 (1920).

belonging to different atoms, by polymerization, perhaps an effect of the heat, does not occur. Then simply in all elements of even numbers all electrons would be coupled, and in odd ones one electron is free; the appendage of free electrons in the envelope would be one positive unit of weight 3 in the nucleus; of course we must then accept the hypothesis spoken of above—that the positive units are compound structures and therefore possibly to be transformed.

In this connexion it is very noteworthy that the lowest elements up to No. 7 follow quite other rules than the others. Isotopes of odd atomic weights play an important part in 3 Li, 4 Be, 5 B, *i. e.*, in the lowest, most positive elements of the first period, but do not occur in 6 C and 7 N. It is here no question of odd or even numbers, but of positive or negative elements; if we assume the units 3 as indicating some free electrons in the envelope, we should have in these lowest elements the very state that I assumed to prevail under normal conditions. It may then be assumed that these elements up to No. 7 belong to a lowest stage, in which the element equilibrium exists only under a small pressure—the following elements of our first stage, 8–20, created under a pressure sufficient to alter the conditions in the outermost layer of the electron envelope, but not sufficient to effect the absorption of electrons into the nuclei. It is obvious that such an outermost layer of the earth would soon cool so that element-reactions could not take place there; then the elements belonging here could no longer be created, but they could be destroyed if they migrated to deeper layers. We find, indeed, these lowest elements up to No. 7 unmistakably rarer than most other elements of our stage 1. Our stage 1 would thus be divided into several stages, the lowest of which reaches to No. 7; if thus No. 8, O commences a new stage, the rule that the lowest element of a stage is rare would not be valid in this low part of the element system.

It is thought by some that elements of an odd number, as a rule, are rarer than even ones. Regarding the higher parts of the system, this would from our standpoint be explained by a greater speed of decomposition in the odd elements at their wanderings in the interior. Yet such a rule does not seem altogether manifest; at least it is rather obscured by the many other causes of rareness in elements. But in Aston's table of isotopes it seems to be manifest that in the higher part of the system there exist, as a rule, only few isotopes of odd elements, but often very many isotopes of even ones. We have said above that many unimportant isotopes may be intermediary products of decomposition,

which then would be further decomposed with a greater speed if they have an odd than if they have an even number.

The reflexions made above have, of course, significance not only with respect to the earth, but to all celestial bodies, and we shall in this connexion examine the data about the specific gravity of the planets. We find the planets, in this respect, belonging to two categories, which are to be examined separately—the small bodies with high density and the big ones with considerably less density obviously depending on the latter still being so hot that they are not bounded by solid crusts, but by envelopes of hot gases.

Regarding the former, the following table shows the values now assumed, the values for the earth being taken as unit :—

	Moon.	Mercury.	Mars.	Venus.	Earth.
Mass	0·012	0·03	0·10	0·79	1
Density	0·62	0·64	0·71	0·79	1

The specific gravity of the earth is so great, 5·6, that it has not been attempted to explain it by the compression, in the interior, of the materials of the crust, but it has been assumed that in the interior of the earth there exists a heavy nucleus of metal, which also is in accordance with the seismologic experiences. Our assumptions above are in agreement with this view, but with the addition that the formation of the nucleus of heavy elements is an effect of the pressure in the interior of the earth. The pressure depends on the mass, and therefore it is to be expected that the greater the mass of a body is, the greater will its density be. In the table above we find, indeed, such a rule conspicuously appearing, and we must regard this table as a good confirmation of our views. The increase of specific gravity with mass would firstly show that the greater the mass the greater the percentage that occupies the heavy nucleus. To explain this unequal distribution of the heavy elements in the several celestial bodies by cosmogonical causes might perhaps be possible in the case of the moon, but in the other bodies it would appear as a mere incomprehensible chance ; by our hypothesis that it is the pressure, and thus the very mass, that creates the heavy elements, the thing becomes plainly intelligible.

The density of the moon (and of Mercury) is not much greater than would be expected of compressed silicates ; still, a small metallic nucleus may be assumed. In Mars it is greater, and still more so in Venus. The difference between Mars and Venus is less than would be expected ; probably

the interior of Mars is cooled down rather much, and is far less hot than the interior of Venus. The seismologists seem to estimate the thickness of the silicate mantle of the earth as about 1500 kilometres; the heavy nucleus would then occupy about 40 per cent. of the total volume. In Venus the outermost layer is, of course, thicker, the percentage of the nucleus less than in the earth; but we have certainly to assume, too, that in the earth the heavy interior layers of the nucleus occupy a percentage of the volume that gives them a considerable influence on the specific gravity of the planet, whilst in Venus their influence is little.

Regarding the big planets, including the sun, which are surrounded by an envelope of hot gases, the matter is more complicated. On the one hand, the pressure, depending on the mass, raises the specific gravity; on the other hand, the temperature of the gaseous surface lowers it. The temperature depends on the degree of cooling at which the body has arrived, and the greater the mass, the less is the speed of the cooling. The mass acts thus in two ways directly opposed to each other. In the cases of the sun and of Jupiter, the effect of the greater pressure and the higher temperature of the sun outweigh each other; the specific weight of the two bodies is well-nigh identical. Uranus, the mass of which is about 5 per cent. of that of Jupiter, has a somewhat lower density than the latter; whilst Neptune, the mass of which is nearly equal to that of Uranus, has a rather high density, probably depending on Neptune, the remotest of the planets, having had a longer time than the others to cool.

Saturn, with about one-third of the mass of Jupiter, has a specific gravity little more than the half of that of Jupiter. This value does not seem to fit into the table, and it is probably to be assumed that some peculiar circumstance has influenced this planet. We may think of the so-called *nova* phenomena. A star blazes up very suddenly, but the brilliancy of it disappears again very soon; it is thus a phenomenon of rather small importance in the history of the star. The most usual explanation seems to be that a body, surrounded by a gaseous envelope that is already somewhat cooled and therefore shining only feebly, by an eruption from within gets the gaseous envelope torn asunder for a moment, so that hot layers in the interior become visible until the envelope has collected again. The old state, however, cannot be totally restored at once; the eruption has transported an appreciable quantity of heat up to the exterior gaseous envelope, which therefore for a considerable time is hotter and thus thinner than that corresponding to the real

equilibrium, and an abatement of the apparent density of the measure that we observe in Saturn might very well be the consequence. It may be emphasized that this very planet has another unique peculiarity too, namely the ring, which, of course, makes it still more probable that Saturn alone among the planets shows the marks of some peculiar agency.

We may finally mention the meteors. These are thought to have come from a planet which eventually became shattered. The meteoric stones would then come from its silicate mantle, the irons from its nucleus. As very heavy metals do not seem to occur there, this nucleus may only have been equivalent to the outermost part of the nucleus of the earth, and the astronomers seem indeed to assume this planet to have been rather small. To explain in detail the composition of the meteoric irons, iron and a little nickel, is difficult, as there seem to exist several possibilities, between which we cannot decide. To mention only one possibility, the asteroid planet may have already cooled so that element-shaping reactions did not occur in the nucleus or the magma basins which the irons came from, and the constituents had then emigrated into the silicates so that beside the main component, iron, there remained only nickel, which, as we have already mentioned, was perhaps hampered in its movements.

Addendum.—In the above paper, in the last section dealing with the astronomical data for the masses and specific weights of the planets, the values (taken from the Almanac for 1928 of the Swedish Academy of Science) vary much in their reliability; this I did not take sufficiently into account, and therefore the following may be added:—

Of the planets bounded by solid crusts the values for the earth, Mars, and the moon, which fit our assumptions well, are certainly exact. For the planets which have no satellites the values are not so trustworthy. The values for Venus still do not vary greatly: it seems certain that both mass and density are somewhat lower than those of the earth, but the value 0.79 for the density is perhaps too low; a somewhat higher value would in reality fit our system better. For Mercury values varying from 0.64 to 3 are to be found; it seems necessary to omit this planet, the data being too variable.

As regards the bodies bounded by envelopes of hot gases, the most probable values for the densities of the Sun, Jupiter, Uranus, and Neptune seem to be about 0.25; the values for Uranus and still more for Neptune are yet somewhat varying; the very different value for Saturn 0.13, as commonly given, is certainly reliable.

LXXXIII. *The Spectrum emitted by a Carbon Plate under Bombardment.* By A. A. NEWBOLD, B.Sc.*

MOST of the experiments on the radiation which fills the gap between the two groups which are amenable respectively to X-ray crystal and ordinary grating methods have dealt with the conditions of excitation of such radiation. As a rule the radiation emitted from various elements under the bombardment of electrons from a glowing filament has been measured by its photoelectric effect on a target of some metal, such as copper, nickel, etc. The accelerating or bombarding potential is usually varied in steps, and the total radiation measured at each step by means of its total photoelectric effect, the latter being determined by some such means as the charging-up of an electrometer connected to the insulated target. These photoelectric currents divided by the corresponding thermionic currents are then plotted against the accelerating voltage producing them. If, now, there is present characteristic radiation superposed upon the general radiation, it is to be expected that at the characteristic voltage which just excites this radiation there will be some kind of a discontinuity, such as a kink or change in slope of the curve.

Whilst the method thus outlined is valuable, it has considerable limitations, and its results require simplification and also restriction by comparing with those given by other methods. In particular, it almost certainly yields discontinuities at potentials which are not excitation potentials, properly speaking, at all †, and it gives no information whatever as to the frequencies or distribution of energy in frequency of the radiation excited. In fact, it tells little or nothing about the character of the spectrum produced.

The method of the present experiments is different. The primary exciting voltage is now kept constant, and, in fact, all the conditions of operation of the part of the tube generating the radiation are kept as constant as possible. The radiation generated is allowed to pass through an appropriate ion filter into an adjacent chamber, where it falls on a small electrode at the centre of a large spherical electrode. An electric field is maintained between the electrodes, and is so directed as to oppose the motion of the photoelectrons ejected from the central electrode. The

* Communicated by the Author.

† For a fuller discussion see O. W. Richardson and F. C. Chalkin, Roy. Soc. Proc. A, ex. p. 247 (1926).

potential difference V between the electrodes is increased or diminished in steps, and the current of electrons is measured which is able to pass through this field to the surrounding electrode. The central electrode being small and the field radial, the condition that an electron ejected with velocity v shall contribute to the current is

$$\frac{1}{2}mv^2 > eV. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The experiment thus determines, at least very approximately, the distribution of kinetic energy among the emitted electrons. But it is well known that when monochromatic radiation of frequency ν falls on a metal, electrons are emitted with all velocities not exceeding the abrupt limit set by the equation

$$\frac{1}{2}mv^2 = h(\nu - \nu_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ν_0 is the threshold frequency of the metal. If our experiment were performed with such a monochromatic radiation, the result would be zero current for all values of

$V > \frac{h}{e}(\nu - \nu_0)$, and for $\frac{h}{e}(\nu_1 - \nu_0) > V > 0$ the current plotted

against V is the function which represents the integration of the energy distribution function with respect to energy. In general, we have to deal with a mixture of a general radiation and a number of monochromatic radiations of frequency ν_1, ν_2 , etc.; so that we expect the experimental curve to arise from the superposition of a number of such curves on the continuous curve due to the general radiation. This curve should have a discontinuous change of slope at each of the

successive values of V equal to $\frac{h}{e}(\nu_1 - \nu_0), \frac{h}{e}(\nu_2 - \nu_0)$, etc.,

and thus enable us to pick out the monochromatic constituents ν_1, ν_2 , etc. present in the radiation. The method might be misleading if the rise of photoelectric current with voltage after passing the critical voltage for monochromatic radiations were very gradual, in which case the discontinuities would be systematically displaced, or if the energy-distribution function for electrons liberated by monochromatic radiation were too complicated, in which case there might be too many discontinuities. However, our present knowledge of such phenomena does not lead us to anticipate the existence of these difficulties, except perhaps as occasional accidents.

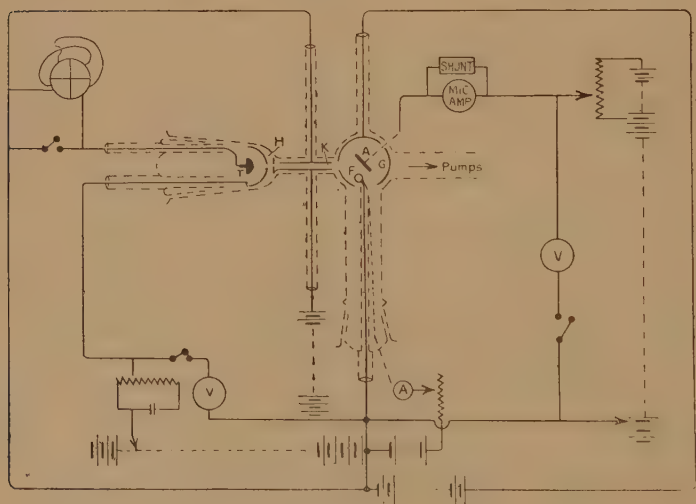
This method was first used in this region of the spectrum by Richardson and Bazzoni*, who tried it in dealing with

* Phil. Mag. xxxii. p. 426 (1916); xxxiv. p. 285 (1917).

the radiations from various gases and vapours. It was not very satisfactory in that application, on account of difficulties introduced by the gases necessarily present. It has since been improved and applied to the detection of soft X-rays by Lukirsky *. The results of the present investigation suggest that it is capable of development into a method of considerable precision.

A plan of the tube is shown drawn to scale in fig 1 *a*. It is made of transparent quartz glass, so that it and the enclosed electrodes can be thoroughly and conveniently baked out. The connecting wires are brought out and soldered to metal

Fig. 1.



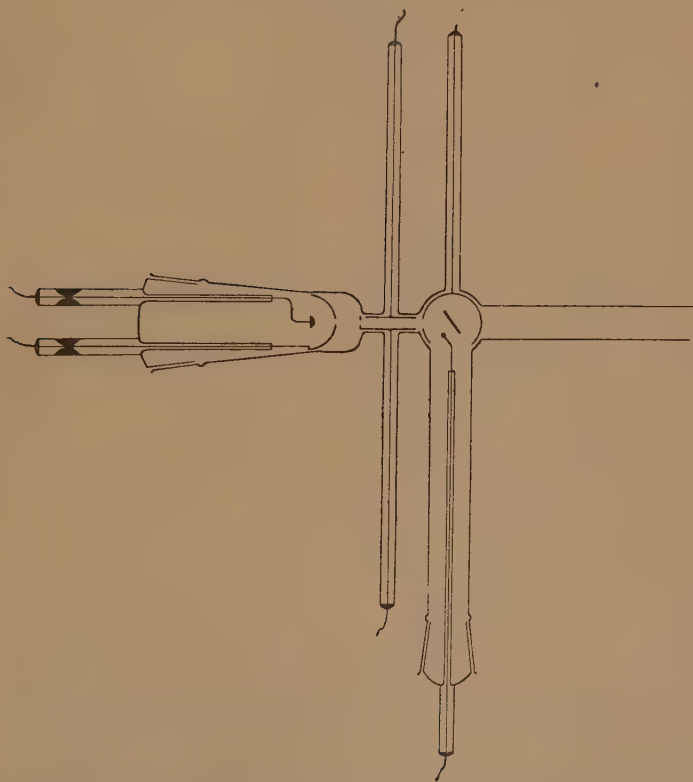
Apparatus.

caps which are cemented to the quartz with sealing-wax. The quartz tube is also connected to the glass connexion of the evacuating apparatus by a sealing-wax joint. The filament F is heated by a set of accumulators with a rheostat and ammeter in series. The accelerating potential from the filament F to the anode A is provided by a large battery of 300 accumulators in series. In order to keep this potential constant, the last section of the accumulators is shunted by a coil of bare wire wound on an open frame, and the potential taken from a contact which can move continuously along

* Phil. Mag. xlvii. p. 466 (1924); *Zeits. f. Physik*, xxii. p. 351 (1924).

the wire and is set so as to maintain a constant reading on the voltmeter connected across the gap FA. This circuit also includes a suitable micro-ammeter for measuring and controlling the thermionic current. The guard electrode is of copper and is cylindrical in shape, with the requisite holes for the escape of the radiation and the admission of the leads and supports for the electrodes A and F. Its function is to

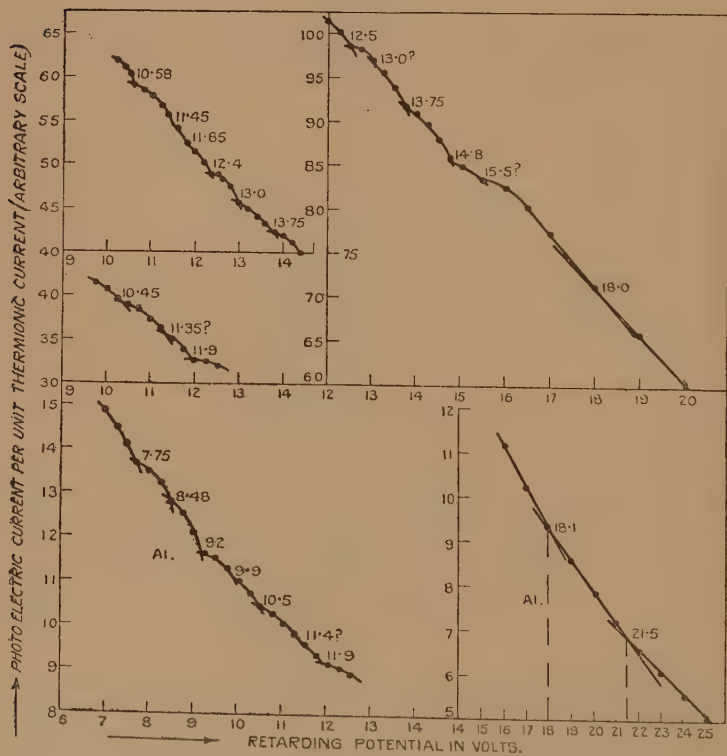
Fig. 1 a.



stabilize the accelerating field, and it is kept at a potential slightly negative with respect to F, so as to drive back any electrons tending to pass into the measuring chamber. The radiation passes through between the condenser plates K. These plates are kept at a potential difference of 200 volts to filter out any ions present in the stream of radiation. The potential difference which it is necessary to apply is ascertained by taking a saturation curve for the current across

the gap between the plates K under the working conditions. The radiation passes through the small rectangular slit in the hemisphere H and strikes the photoelectric target T which is connected to one pair of quadrants of an electrometer. Both the electrode H and the target T are of copper. The retarding potential is applied between H, and the other pair of quadrants of the electrometer from dry cells, a fine adjust-

Fig. 2.

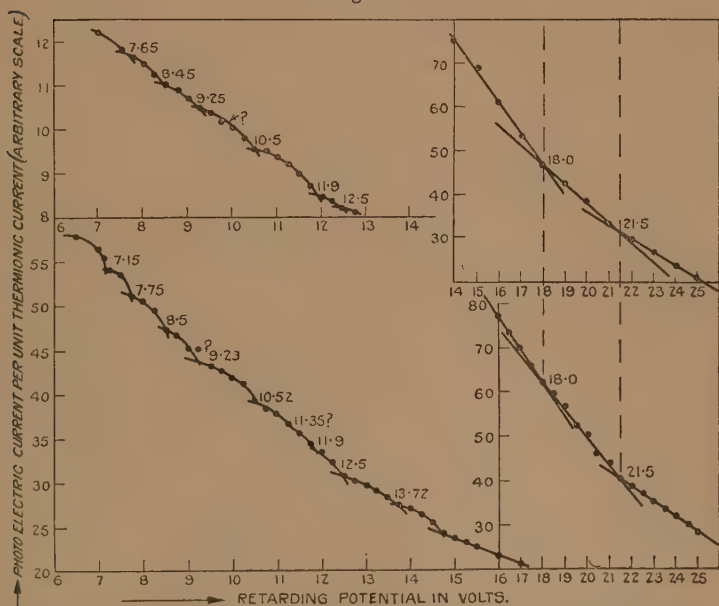


ment being provided by means of a potentiometer across a 2-volt accumulator. All the electrostatic measuring apparatus and connexions are shielded in the usual way. The apparatus is exhausted during operation by means of an ordinary backing pump, a rotary oil pump, a mercury vapour pump, and two liquid air traps, the last one being filled with charcoal. These evacuating devices are all in series.

The element chosen for the present investigation was carbon, the target T being cut from an arc lamp carbon and

having the dimensions $16 \times 10 \times 1.5$ mm. The apparatus was first of all highly exhausted, and the vacuum kept up by running the pumps during the readings. The quartz tube was then baked out properly to drive out occluded gas, and the anode for the same purpose brought to a red-heat several times by bombarding from the filament with about 3000–4000 volts obtained from a transformer. After this the filament current was switched on and a constant accelerating potential, which was usually 300 or 600 volts, was applied. The filament current was adjusted, and through it the

Fig. 2 a.

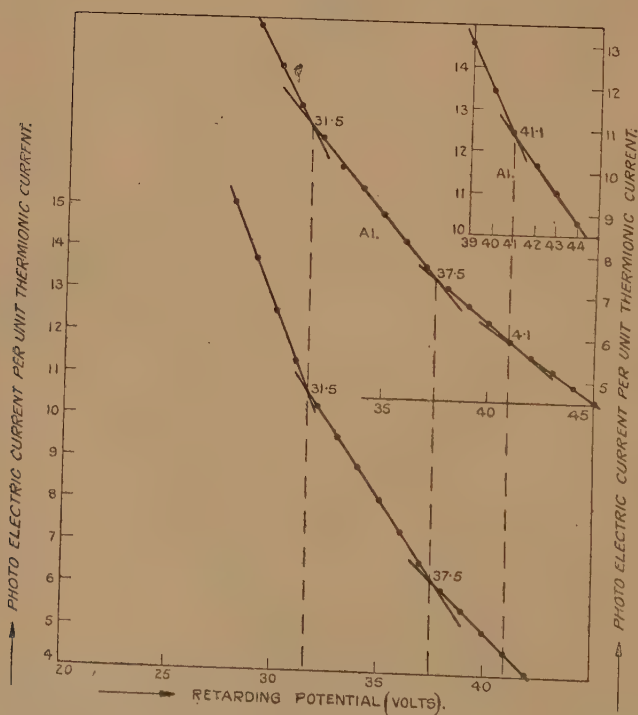


thermionic current, so that the rate of deflexion of the electrometer was most suitable for accurate measurement. The whole apparatus was then left until any more gas which might have been driven off from the filament and other parts of the apparatus near it had been removed and the high vacuum was steady, and until the thermionic current had been steady for some time. As a rule, the tube was run for one or two hours before taking observations, and no readings were taken unless a vacuum of between 10^{-7} and 10^{-8} cm. was attained and electrical conditions steady; under these conditions readings were entirely reproducible. The photoelectric current for varying retarding potentials was then

observed and a curve plotted between these variables. At first the voltage was varied in steps of one or two cells, these being reduced latter to 1 volt, $\frac{1}{2}$ volt, and $\frac{1}{4}$ volt, and ultimately to $\frac{1}{10}$ volt. The current was measured by timing the deflexion of the electrometer whose sensitivity was 1400 divisions per volt.

With the apparatus as described the deflexion of the electrometer is, in general, in the opposite direction from that

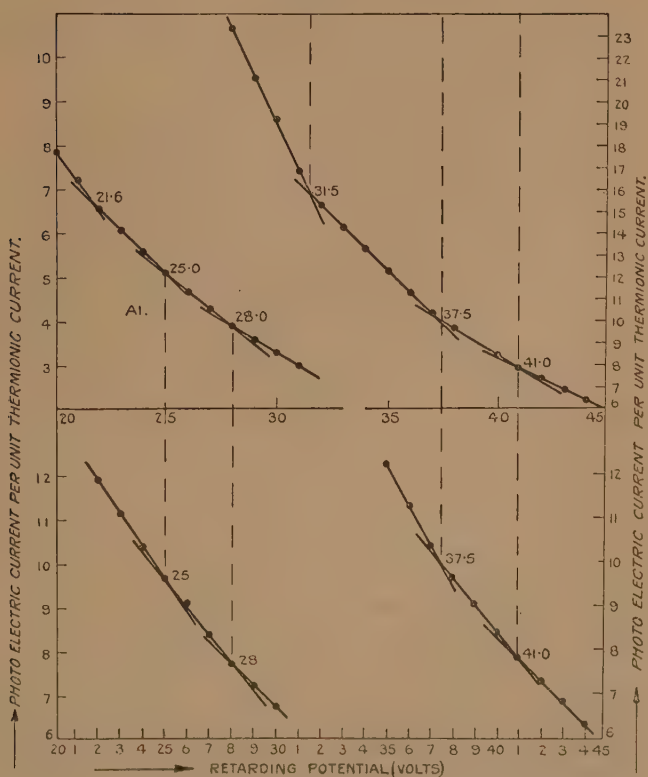
Fig. 3.



to be anticipated from the considerations which have hitherto been brought forward. This appears to be due to electrons emitted by the photoelectric action of the radiation on the edges of the slit in H and the adjacent ends of the condenser plates K. The current is composed of the true photoelectric current and electrons from the outer electrode which are driven by the field on to the target. This latter opposes the true current, and with any but low retarding potentials swamps it so as to give an apparent "positive" effect. At

any rate, this trouble has been removed by putting one of the plates K at zero potential and the other at a positive potential. The end of the positively-charged plate is then bent round at right angles and a slit cut in it rather smaller than the slit in H. The effect of these measures is to prevent the radiation from reaching the edges of the slit H and to introduce a retarding field for electrons between H and K.

Fig. 3 a.

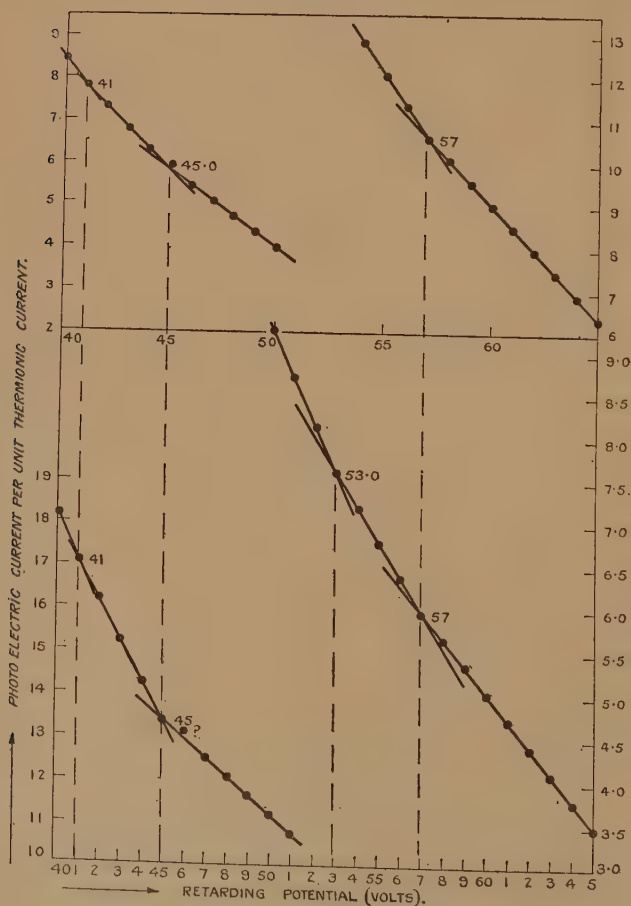


Under these conditions the effects observed are remarkably sharp and entirely reproducible, and the observed discontinuities seldom appear to vary in position by $\frac{1}{10}$ volt.

Some of the results are exhibited in figs. 2-4. Figs. 2 and 2 a contain the phenomena from 6 to 25 volts, figs. 3 and 3 a those from 20 to 45 volts, and figs. 4 and 4 a those from 46 to 65 volts. In all these plots every single experimental point is marked; there are no omissions or other

corrections or adjustments. Below about 15 volts it will be observed that the graphs consist of intersecting portions of curves which are individually concave to the voltage axis; above 15 volts this feature disappears, the curves becoming intersecting straight lines.

Fig. 4.



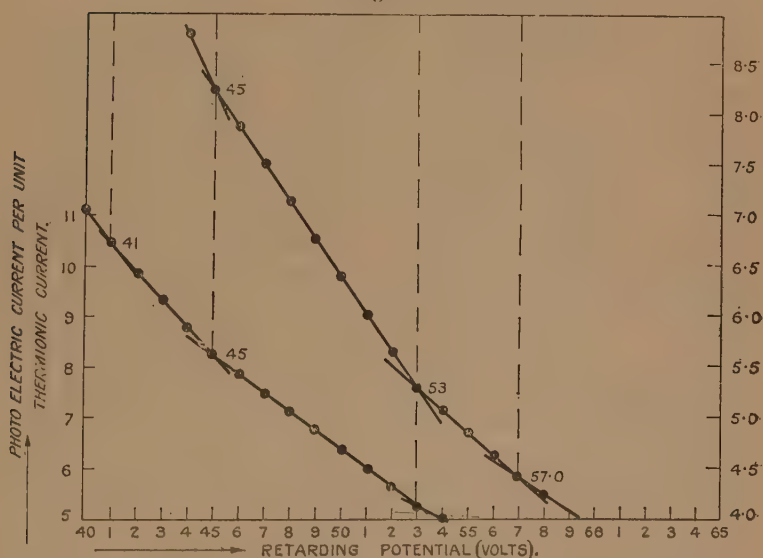
Let K be the contact potential difference between T and H , and let ν_0 be the threshold frequency of the material of T ; then if there is, in the radiation falling on T , a monochromatic constituent whose frequency is ν_s , we shall, according to the foregoing discussion, expect a discon-

tinuity in graphs such as those of figs. 2-4 *a* at the potential V_s , as read on the voltmeter, which satisfies

$$e(V_s + K) = \frac{1}{2}mv^2 = h(\nu_s - \nu_0), \dots (3)$$

$V_s + K$ being the actual potential difference which reduces the maximum velocity of electrons liberated by this radiation to zero; so that the frequencies of the monochromatic radiations should be given for every V_s by

$$\nu_s = \nu_0 + \frac{e}{h}(V_s + K). \dots (4)$$

Fig. 4 *a*.

The value of ν_0 for copper has been measured by Richardson and Compton * as 10^{15} sec.⁻¹, or the equivalent of 4.12 volts. As the surfaces both of T and H were of copper in the experiments, we should anticipate that K would be zero, so that the observed V_s would require correction by the addition of the quantity of $\frac{h}{e}\nu_0$ or 4.12 volts.

Before adding this correction, however, these measures were compared with the frequencies of the lines of the carbon spectrum in the part of this region where they have

* Phil. Mag. xxiv. p. 586 (1912). There is a second determination giving a value 3 per cent. lower.

been found and measured by Millikan and Bowen on the vacuum grating spectroscope. It is to be remembered that Millikan and Bowen's spectrum was generated by hot sparks between arc carbon electrodes, and is therefore presumably that of an electrically-excited gas of more or less familiar type. There does not appear to be any *a priori* method of knowing how close a correspondence to anticipate between such a spectrum and that generated by the impact of electrons on the same substance in the solid state. It was rather surprising to find that the spectrum was coincident with that of Millikan and Bowen, provided no correction whatever was made for the work done by the electrons in getting out of the copper. This can be seen from Table I., in which the first column gives the critical voltages as measured without any correction, and the second and third columns are the corresponding wave-lengths and wave-numbers as given by the quantum relation. The fourth column contains the lines or groups of lines (where the resolution is insufficient) from Millikan and Bowen's table, which are close to these discontinuities. The last column gives the difference between their numbers and the corresponding measures obtained in these experiments. Of the 76 lines between $\nu=54,561$ and $\nu=277,408$ attributed to carbon by Millikan and Bowen, only 25 are contained in Table I., but they include every line of intensity greater than 6 and most lines of any outstanding strength compared with neighbouring lines anywhere in that spectrum. Except for the three lines of highest frequency corresponding to discontinuities at 25.0, 28.0, and 31.5 volts, there is no discrepancy amounting to as much as 0.2 volt. Even at the three highest frequencies corresponding to 25.0, 28.0, and 31.5 volts the discrepancy is not very great. The exact values for the weak inflexions at 25.0 and 28.0 volts may be difficult to ascertain, and there is something peculiar about the inflexion at 31.5, which was not resolved from 37.5 in the earlier observations, although it should have been as far as one could expect. If the above measures and Millikan and Bowen's are plotted on two scales, it does not seem possible to effect any similar set of coincidences in any other position obtained by sliding the scales past each other. Such a movement would correspond to the addition or subtraction of a linear correction such as that for the work function of copper. It appeared then, at first, as if the discontinuities occurred at voltages which, without any correction, were equivalent on the quantum relation to Millikan and Bowen's frequencies.

On examination of some of the earlier curves it was noted that for the low retarding potentials no drop in the photo-electric current was observed until a retarding potential of 4.1 volts had been reached, when the current immediately

TABLE I.

Volts (V _s).	λ (Å.U.).	ν (wave-number).	Millikan & Bowen. ν (Int.).	Diff.
(ν_0 for Cu.)	4.12	3,000		
weak.	7.05	1752	5,706.8 (2)	— 1.8
	7.66	1613	{ 6,032.8 (5)	+ 167.8
			{ 6,404.8 (5)	— 204.8
	8.47	1459	6,832.0 (2)	+ 18.0
	9.23	1338	{ 7,490.9 (15)	— 10.9
			{ 7,554.4 (7)	— 74.4
weak.	9.88	1250	8,015.8 (7)	— 15.8
	10.51	1174	8,506.2 (15)	+ 3.8
weak.	11.4	1083	{ 9,152.2 (3)	+ 77.8
			{ 9,381.2 (8)	— 151.2
	11.88	1030	{ 9,646.1 (11)	+ 63.9
			{ 9,899.0 (10)	— 189.0
	12.47	992	10,234.3 (12)	— 154.3
weak.	13.0	10,515	10,575.2 (4)	+ 60.2
	13.71	901	11,060.6 (10)	+ 39.4
			{ 11,648.1 (5)	+ 271.9
			{ 11,787.6 (0)	+ 132.4
	14.74	838	{ 12,346.4 (5)	— 426.4
			{ 12,395.7 (6)	— 475.7
			{ 12,501.6 (5)	— 581.6
	18.0	687	14,549.1 (8)	— 9.1
	21.5	575	17,405.2 (6)	— 5.2
weak.	25.0	20,250	20,014.0 (4)	+ 236.0
weak.	28.0	22,660	21,755.2 (6)	+ 904.8
strong.	31.5	25,500	25,882.6 (4)	— 382.6
strong.	37.5	30,380		
	41.0	33,200		
strong.	45.0	36,450		
strong.	53.0	42,900		
	57.0	46,200		

began to drop. Further experiments showed that there was a constant accelerating force superimposed on the retarding field of the sphere by the positive potential on the condenser plate and shield. This, by a strange coincidence, was almost exactly equal to the threshold value V_0 of 4.12 volts. (This held whether the target was made of copper or of aluminium,

as is mentioned later.) There was present, in fact, a state of affairs akin to the plate and grid of a thermionic valve. This effect then just balanced the threshold function and made any correction of the recorded values unnecessary.

In the foregoing it has been assumed, to simplify the discussion, that the electrons emitted from the electrode T were ejected, by the radiation from the carbon target, from the superficial levels which supply the electrons in the photoelectric effect as ordinarily observed in the ultra-violet. They might, however, arise from the action of X-rays of higher frequency, let us say ν_c , from the carbon target on electrons in the M-level of copper, in which case the observed discontinuities would be at voltages equivalent to $h(\nu_c - \nu_{m_1})$, $(\nu_c - \nu_{m_2})$, etc., where ν_{m_1} , ν_{m_2} , etc. are the frequencies corresponding to the M-thresholds for copper. In such a case the voltages of the observed discontinuities would depend on the material of T as well as of the target A. This matter has been put to the test by repeating all the observations with an aluminium electrode at T instead of the copper electrode. Some of the curves so obtained are shown in figs. 2-4 a, marked Al. It will be seen that the discontinuities occur at exactly the same place with the aluminium as the copper electrode. At first sight it might be thought that even if the electrons were generated from the most superficial levels, the apparent discontinuities would be shifted owing to the introduction of the contact-electromotive force between aluminium and copper. This is not the case, however, for the effect of the contact potential difference in reducing the energy of the emitted electrons is just counterbalanced by the extra energy got owing to the reduced work function, with the result that the stopping potential with illumination of assigned frequency is independent of the nature of the metal illuminated*. All the discontinuities given in Table I. are present both with the copper and with the aluminium electrodes, except that the three weak inflexions at 7.05, 9.88, and 11.4 volts have not been recognized on the aluminium graphs. This does not necessarily prove that they are specific to copper, as they are not detectable on all the copper graphs. The rest must without doubt be carbon lines. Most of the measurements have been made with 600 volts on the X-ray generating tube, but many sets have been taken at 480, 300, and 240 volts, and one determination of the discontinuities below 20 volts has been made with 120 volts only between F and A in fig. 1.

* Richardson & Compton, *Phil. Mag.* xxiv. p. 575 (1912).

Summary.

This paper describes an electrostatic method of investigating soft X-ray spectra and its application to the spectrum emitted by a carbon plate under electron bombardment up to 600 volts. Over the frequency range 5700 to 26,000 the spectrum found is either identical with or at least resembles very closely that mapped by Millikan and Bowen for gaseous carbon.

In conclusion the writer wishes to express his thanks to Dr. H. T. Flint, who assisted in the early stages of the work.

LXXXIV. *The Magnitude of Non-Dimensional Constants.*

By W. N. BOND, M.A., D.Sc., F.Inst.P., *Lecturer in Physics in the University of Reading* *.

THE problem here discussed may have been considered before by other writers, but absence of any treatment of, or definite reference to work on, the subject in current Physics literature is thought to be sufficient to justify the present paper †.

The "constants" occurring in physical equations may be classified thus :—(1) Universal constants, such as the velocity of light in a vacuum ; (2) specific constants, such as the thermal conductivity of copper ; (3) arbitrary constants, such as the number of degrees in a right angle ; and (4) numerical constants, such as $3/2$, π , $\sqrt{2}$. This last type of constant is the one here considered.

These numerical constants occur as multiplying factors in equations such as that for the volume of a sphere

$$V = \frac{4}{3}\pi r^3,$$

and are very often ratios geometrical in their origin. They may sometimes be less easily deduced theoretically, as in the case of the capacity of a pair of conducting spheres placed in contact but at a distance from other bodies. The form of the equation may frequently be predicted from dimensional considerations ; and it might be convenient if the order of

* Communicated by the Author.

† Reference may be made to Einstein, *Ann. der Physik*, xxxv. p. 687 *et seq.* (1911).

magnitude of the constant involved could also be predicted before it was obtained by detailed theory or experiment.

It is known from experience that these numerical constant multiplying factors do not often differ very greatly from unity in value. Also it is known that, for any one greater than unity, there is automatically the reciprocal value less than unity. If, with the values of the numerical constants as abscissæ, a frequency distribution curve be drawn, it will be skew and limited in one direction (at zero). If the logarithms of the constants had been used as abscissæ, a symmetrical curve extending to infinity in both directions would have been obtained.

For the construction of the curve, the numerical constant multiplying factors (including unity) were collected by random selection from physical equations from eleven different sources, giving 731 values above unity (and their reciprocals below unity). It was found that the fraction falling between 2 and $1/2$ in value was 733/1462 (*i. e.*, differing from $1/2$ by less than the error of sampling). Using Peters's formulæ, it was attempted to fit a normal law of errors curve to the symmetrical distribution obtained by taking the logarithms of the constants as abscissæ. The curve thus obtained corresponded to half of the constants falling between 2.18 and 0.459 in value. It was found, however, that the observations were definitely in better agreement with the following hypothesis:—that the constants less than unity were distributed in value uniformly between 0 and 1 (with the corresponding distribution from 1 to ∞). This theory is compared with the experimental results in the following table:—

Range of values of the constants.	Calculated.		Observed.
	Fraction in the range.	Number in the range.	Number in the range.
0 to $1/3$	$1/6$	243.7	245
$1/3$ to $2/3$	$1/6$	243.7	237
$2/3$ to 1	$1/6$	243.7	249
1 to 2	$1/4$	365.5	366.5
2 to 4	$1/8$	182.8	187.5
4 to 8	$1/16$	91.4	95
8 to 16	$1/32$	45.7	42.5
16 to 32	$1/64$	22.8	25
32 to 64	$1/128$	11.4	11.5
64 to ∞	$1/128$	11.4	3

Apart from the fact that the proposed theory predicts rather more values over 64 (and similarly under $1/64$ th) than were observed, the observations and theory are in very close agreement. This agreement and the very simple nature of the suggested law make it seem likely that, in general, this law is applicable to the non-dimensional numerical (but not arbitrary) constants which occur as multiplying factors in equations arising in physical calculations. (It is not suggested that the law applies to the numerical multiplying factors which occur in the various terms of an expansion in the form of a mathematical series.) The probability, then, of any such constant chosen at random falling in value outside the range ($1/3$ to 3) is $1/3$, and so on.

University of Reading,
Department of Physics.
7th January, 1929.

LXXXV. *A Complex Pendulum driven by Two Pendulums having Commensurate Periods.* By H. M. BROWNING, *M.Sc., Ph.D.**

[Plates XVI. & XVII.]

IN previous papers † the author has analysed theoretically and verified practically the motions set up in pendulums when two or more were coupled together. Also the effect of resonance has been shown when one or more pendulums have acted upon several responders. In the latter, either the aggregate effect over a long period or the instantaneous effect has been obtained. No record of the actual motion with time of one pendulum has been shown. In connexion with a practical problem, it was thought desirable to have such a record, and so the work described below was undertaken. Thus in the present instance the aim was to obtain records of a complex pendulum when it was subjected to external vibrations of different frequencies acting at the same time. During one set of experiments the ratio of the periods of the compound-responding pendulum was kept constant, as well as the ratio of the driving pendulums, but the actual periods of the latter were altered between wide limits.

These pendulum experiments reproduce the motion of phase swing that will take place in a synchronous electrical

* Communicated by the Author.

† *Phil. Mag.* (6) xxxiv. pp. 246-270 (Oct. 1917); xxxvi. pp. 169-178 (Aug. 1918); xxxvii. pp. 453-455 (April 1919); xlv. pp. 573-576 (Sept. 1922).

machine subjected to a periodically fluctuating load. It is well known that an alternator working in parallel with other alternators is subject to such phase swinging, and that the period of the swing is a definite quantity which can be calculated with fair accuracy for any given machine. The same also applies to a synchronous motor and to a rotary-converter which is fed on its A.C. side. This latter machine, particularly, is subject to fluctuating loads, especially when it is used for traction work.

In practice, the load curve will consist of a number of sharp, unrelated peaks, but occasionally it happens that a series of such peaks may occur at fairly regularly-spaced intervals. In such a case the load will correspond to a sinusoidal load whose period is fixed by the time interval between the successive peaks, with a number of harmonics superposed. The mechanics of the machine is thus similar to that of a pendulum having definite free periods acted on by a series of forces with periods in the ratio $1 : \frac{1}{2} : \frac{1}{3}$, etc. The amplitudes of all but the fundamental and one of the harmonics may be in some cases negligible, and then the motion is that of a pendulum acted upon by two external forces having commensurate periods.

Experiments on the rotary-converter loaded in this manner have shown that the motion of phase swing is very similar to that of the pendulums previously described, especially if the damping of the rotary-converter is small, as it was in the experimental machine.

Theory.

The complex pendulum was made on the principle of the cord and lath pendulum described in the Phil. Mag., Oct. 1917.

At the end of a long light wire a small loaded aluminium bucket, with a hole in the bottom, was attached. At a fixed point on the wire a weight was fastened. Salt was allowed to run slowly from the bucket, and the weights and lengths adjusted so that, when vibrating freely, the pendulum oscillated with two frequencies, which were in a simple ratio, and which remained approximately constant in spite of the loss of salt (this is considered more fully later).

Using the same notation as in equations (55) and (56), p. 259, Phil. Mag. xxxiv. Oct. 1917, the two following equations are obtained for the motion of the pendulum :

$$P \frac{d^2 y}{dt^2} + P m^2 y = P m^2 \alpha z, \quad (1)$$

$$Q \frac{d^2 z}{dt^2} + \{ (P \alpha + Q) n^2 + P \alpha^2 m^2 \} z = P m^2 \alpha y. \quad . (2)$$

As solution

$$y = e^{xt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$z = \frac{x^2 + m^2}{m^2 \alpha} e^{xt}. \quad \dots \dots \dots (4)$$

Then

$$Qx^4 + Qm^2x^2 + \{(P\alpha + Q)n^2 + P\alpha^2m^2\}x^2 + \{(P\alpha + Q)n^2 + P\alpha^2m^2\}m^2 = Pm^4\alpha^2,$$

i. e.

$$x^4 + \{(\mathbb{M}\alpha + 1)n^2 + (\mathbb{M}\alpha^2 + 1)m^2\}x^2 + (\mathbb{M}\alpha + 1)m^2n^2 = 0, \quad (5)$$

where

$$M = P/Q.$$

Thus, if $\pm ip$ and $\pm iq$ are the roots of equation (5),

$$p^2 + q^2 = (M\alpha + 1)n^2 + (M\alpha^2 + 1)m^2,$$

$$pq = \sqrt{(M\alpha + 1) \cdot mn} ;$$

$$\therefore p+q = \sqrt{\{(M\alpha+1)n^2 + (M\alpha^2+1)m^2 + 2mn\sqrt{(M\alpha+1)}\}},$$

$$p - q = \sqrt{\{(\mathbf{M}\alpha - 1)n^2 + (\mathbf{M}\alpha^2 + 1)m^2 - 2mn\sqrt{(\mathbf{M}\alpha + 1)}\}}.$$

If $\alpha = 1$,

$$\frac{p}{q} = \frac{\sqrt{\{(M+1)(n^2+m^2)+2mn\sqrt{(M+1)}\}} + \sqrt{\{(M+1)(n^2+m^2)-2mn\sqrt{(M+1)}\}}}{\sqrt{\{(M+1)(n^2+m^2)+2mn\sqrt{(M+1)}\}} - \sqrt{\{(M+1)(n^2+m^2)-2mn\sqrt{(M+1)}\}}}. \quad (6)$$

Values of M , m , and n can be chosen to make the ratio p/q whatever is desired, and in the most suitable manner.

The actual position at time t of the bucket would be given by a formula of the form

$$y = E \sin (pt + \epsilon) + F \sin (qt + \phi), \quad . \quad . \quad . \quad (7)$$

the values of E , F , ϵ , and ϕ being determined by the initial conditions.

No damping factor is introduced into the above equations, as this was found to be negligible with the apparatus used.

Now, if two impressed forces of value $G \sin \omega t$ and $H \sin x \omega t$ are applied to this complex pendulum, we can consider the latter as having two free periods of frequencies

$\frac{p}{2\pi}$ and $\frac{q}{2\pi}$

The equation of motion of this pendulum is

$$\left. \begin{aligned} P\ddot{y} + Pm^2y - Pm^2z &= F \sin \omega t + G \sin x \omega t, \\ Q\ddot{z} + \{(P+Q)n^2 + Pm^2\}z - Pm^2y &= F \sin \omega t + G \sin x \omega t. \end{aligned} \right\} \quad (8)$$

It would be found that the solution of these equations would be of the following form:—

$$\left. \begin{aligned} y &= A \sin (\omega t + \alpha) + B \sin (x \omega t + \beta) \\ &\quad + C \sin (pt + \gamma) + D \sin (qt + \delta) \\ \text{and } z &= A' \sin (\omega t + \alpha') + B' \sin (x \omega t + \beta') \\ &\quad + C' \sin (pt + \gamma') + D' \sin (qt + \delta'). \end{aligned} \right\} \quad (9)$$

z and y give the motion of the bob and the bucket; thus, as the motion of the latter is the only one required, we need not consider the second equation of (9).

The values of the constants A, α, B , etc., may be obtained from equation (8). If ω or $x\omega$ is equal to p or q , resonance will occur, and the effect of this vibration will be so great that any others will be masked.

If damping had been taken into consideration, equation (9) would have required a slight alteration, as p and q would have been modified by the damping factor.

Experimental Arrangement.

The apparatus shown in fig. 13, Pl. V., "Coupled Vibrations," Phil. Mag., July 1918, was adapted for the response of a complex pendulum to two drivers. Figs. 1 and 2 give the side and end elevations of the actual arrangement used. Two stout cords ACB and DEB, as shown in fig. 1, are arranged to be parallel between E and B. At C and E pendulums M and N, with heavy bobs (approximately 2 kilograms), are hung. At S there is a light inflexible stay; at the middle of this is slung the light complex pendulum R, as shown in fig. 2. Under R a board is drawn along, so that a record of the lower bob of R can be made by salt which runs from it.

The point C was placed over a trap-door in the Research Room, so that the length of the pendulum could be increased to give a period of 6 seconds. The pendulum with the short period could be altered from a period of 0.6 of a second to 2 seconds.

The bucket was loaded round the centre with lead shot, so as to make the total mass 40 grams when half filled with salt. The upper bob of the pendulum was made of a ball of plasti-

cine, through which the wire was passed; the ball weighed 40 grams, and was placed three-quarters of the way from the suspension to the bucket. This, after slight adjustment, gave frequencies in the ratio 3 : 1.

Fig. 1.

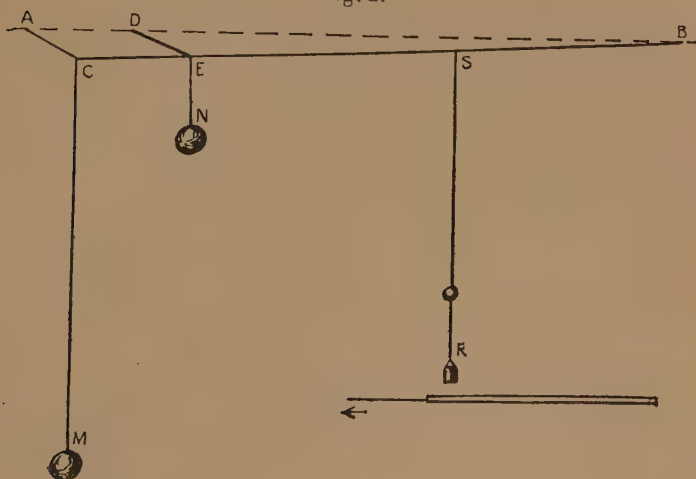
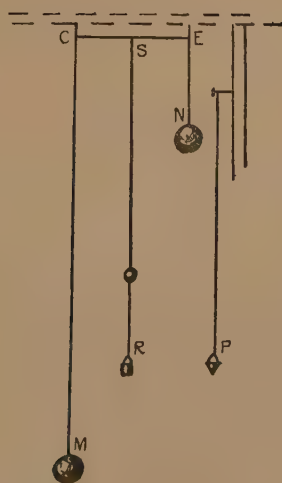


Fig. 2.



In order to obtain the ratio of the frequencies 2 : 1, the weight of the upper bob was made five times that of the lower, and it was placed in approximately the same position as above.

The loss of salt made it desirable to have the total weight of the bottom bob appreciable, or the alteration in the ratio of the periods during an experiment was very marked. It was calculated that for $p/q=3$, with mean $M=1$, for the bucket to start full of salt, and lose it all, the ratio of the periods changed from 2.7 to 3.3. It was found that during an experiment about one-third of the salt in the bucket was run out, so records were taken when the salt was running out from the middle, and this gave an alteration in the ratio of the frequencies of about 5 per cent. When the mean ratio of the frequencies was 2:1, the alteration during the experiment was about 2 per cent.

Calculations showed that the centre of gravity of the bucket, which, when full or empty, was at the geometrical centre of the bucket, was lowered by about one-tenth of the depth of the bucket when half empty. This lengthening of the longer component of the pendulum made about 2 per cent. difference in the ratio of the frequencies, but it could be arranged to make p/q slightly more constant.

At the side of the complex pendulum, about a foot away, a simple pendulum P, having a period equal to the longer period of the first pendulum, was fixed to a rigid support. This was made to oscillate in the same plane as the first pendulum, and a record of its motion was made by salt issuing from a small hole in the funnel which formed its bob.

The record of its motion was used to check the periods of the complex pendulum.

Results.

In the photographic reproductions, the traces of the simple pendulum are always at the top, and since the motion of the board was from right to left, the traces start at the left and finish at the right.

In figs. 1 to 8 (Pl. XVI.) the ratio of the free vibrations of the complex pendulum was 3:1 approximately, the actual periods being 2.2 seconds and 0.715 of a second. In figs. 9 to 20 (Pl. XVII.) the ratio of the free vibrations of the complex pendulum was 2:1, the actual periods being 2.08 and 1.04 seconds.

Figs. 1 and 9 were obtained by keeping the driving pendulums still and allowing the driven one to oscillate with its own free periods. In both cases the motion was started by giving a blow to the upper bob. In fig. 1 it will be seen that the ratio of the vibrations is approximately 3:1, and in fig. 9 the ratio is about 2:1; but in neither case is the ratio quite constant, as is seen by the slight displacement of the

kink towards the end of the trace. It has been explained earlier that it is difficult to eliminate this because of the alteration in the weight of the lower bob due to the loss of salt.

Figs. 2 to 8 are taken with the ratio of the periods of the responder as 3:1, and with the periods of the drivers also in the same ratio. The actual periods of the latter are changed; originally the long driver has a period less than that of the greater period of the responder, and, finally, the short driver has a period greater than the long period of the responder.

Table I. shows the actual periods of the driver corresponding with the figures on Pl. XVI. The periods of the responder are 2.2 seconds and .727 of a second.

TABLE I.

No. of Figure.	Periods of Drivers.	Remarks.
1	None.	Responder started by blow to upper bob.
2	2.13 sec. and .710 of a sec.	} The two periods are seen distinctly.
3	2.15 sec. and .707 of a sec.	
4	2.2 sec. and .73 of a sec.	Trace unmanageable, due to resonance.
5	2.4 sec. and .8 of a sec.	Only slight indication of shorter period.
6	5.85 sec. and 1.95 sec.	In 5, 6, and 7 beating due to free period of responder.
7	1st half 1.95 sec. 2nd half 5.85 sec. and 1.95 sec.	} Traces show that the longer period has no effect.
8	5.85 sec. and 2.2 sec.	

If the ratio of the free periods of the responder is the same as that of the drivers, then about the point of resonance for the two vibrations the response is about equal for each. At any other point of resonance, the vibration due to one period only is apparent, this period being equal to one of the responder's periods.

Table II. gives the results with a responder of periods 2.08 and 1.04 seconds, that is, in the ratio 2:1. The drivers were in the ratio 3:1.

728 *A Complex Pendulum driven by Two Pendulums.*

In all cases the damping of the responders is small ; this prevents the driving pendulums from forcing their own periods on the responders. Thus, when the periods of the

TABLE II.

No. of Figure.	Periods of Drivers.	Remarks.
9	None.	Responders started by blow to upper bob.
10	1·84 sec. and ·613 of a sec.	{ Free periods of responders very pronounced.
11	1·95 sec. and ·65 of a sec.	
12	2·08 sec. and ·69 of a sec.	Long-period driver in resonance with long-period responder.
13	2·40 sec. and ·80 of a sec.	Free periods of responders present.
14	1st half ·80 of a sec. only ; 2nd half 2·40 sec. only.	In second half, beats due to free and forced vibrations.
15	3·12 sec. and 1·04 sec.	Short-period responder in resonance with short-period driver.
16	4·16 sec. and 1·39 sec.	Analysed by Harmonic Analyser—see below.
17	1st part 4·16 sec. only ; 2nd 1·39 sec. added ; last 1·39 sec. only.	Driver with long period has very small effect.
18	5·64 sec., 2·08 sec.	Short driver in resonance with responder of long period.
19	5·64 sec., 1·88 sec.	Shows beats due to responder having free period slightly different from that of one driver.
20	5·65 sec., 1·88 sec.	Made periods of responders 1·85 sec. and ·925 of a sec. Response due to short-period driver only.

driver and the driven are the same, very strong resonance occurs. This may be seen from figs. 4, 12, and 15 ; but, when they are out of tune, it may happen that the responder will vibrate with its own free periods, and also those forced on it by the drivers. This is seen very

strikingly in fig. 16. On examining the trace with the harmonic analyser, the following results were obtained :—

Period of Vibration.	Relative Amplitude.
4·16 sec.	33
2·08 „	100
1·39 „	73
1·04 „	28

The largest amplitude is shown as 100. Thus it is seen that the long free period is the most intense, and the short free period the least intense of the vibrations present.

These effects would no doubt be greatly reduced by damping the responding system, so that the free vibrations were only present for ten or twenty oscillations. However, as the work was undertaken to illustrate what would occur in a machine with free periods of its own, worked by external forces, it is probable that the photographic reproductions of the vibrations made by the pendulums is a good example of the type of motion of the electrical machine.

I should like to thank Mr. H. Cotton, M.B.E., M.Sc., A.M.I.E.E., for giving me some notes about the rotary-converter, on which he has been working, and for suggestions in connexion with this paper.

Nottingham.
Dec. 28, 1928.

LXXXVI. *On the Spectra of Alkali Metals excited by Active Nitrogen.* By J. OKUBO and H. HAMADA (*from the Laboratory of Physics, Sendai, Japan*) *.

[Plate XVIII.]

Introduction.

A PREVIOUS communication† on the results of an investigation of spectra emitted from various metallic vapours in contact with the stream of the active modification of nitrogen gas dealt primarily with the determination of the highest levels of the spectral terms which were excited by the gas. In the course of the experiments, as Lord Rayleigh and A. Fowler‡ have already remarked, a very interesting phenomenon was observed in the case of sodium vapour. When metallic sodium is heated in the side bulb

* Communicated by the Authors.

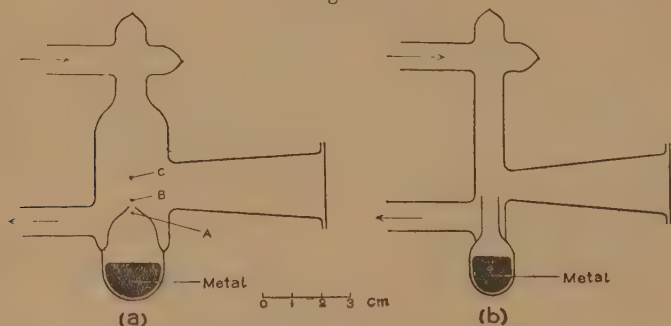
† J. Okubo and H. Hamada, *Phil. Mag.* v. p. 372 (1928).

‡ R. J. Strutt and A. Fowler, *Proc. Roy. Soc.* lxxxvi. p. 105 (1912).

connected with the after-glow tube, a bright green light column is visible in the neck of the bulb where the dense vapour meets the stream of active nitrogen, and surrounding this column a broad yellow aureole diffuses in a large volume. Spectroscopic observation shows that the subordinate series appears with great intensity in the inner green column, while the principal series is strongly visible in the outer diffused aureole. It was remarked in our former paper that this difference in these colours depends absolutely on the density difference between the vapour in the central column and that in the outer aureole.

In this paper the results of further continued observation of the dependence of the spectral line on the density of the vapour of sodium are reported. It has also been confirmed that when a dense vapour of sodium is in contact with active

Fig. 1.



nitrogen, the band spectrum due to the sodium molecules comes into view in addition to the line spectrum, and, on a further increase of the vapour density, an excitation of the band spectrum due probably to the sodium nitride results.

A similar phenomenon was also observed in the case of vapours of both potassium and caesium.

Experimental Arrangements.

In order to study the dependence of the spectral terms on the density of the vapour precisely, the following types of after-glow tube, as shown in fig. 1 (a) and (b), were used. Tube (a) is made of Pyrex glass, its diameter being 2.5 cm. and height about 10 cm. On heating the bottom of the tube, the vapour of the contained metal issues from the nozzle into the stream of the active nitrogen. The diameter of the nozzle was generally about 2 mm. It is possible to vary the pressure of the vapour at the nozzle and at any point in

the tube by selecting a nozzle of a requisite diameter and adjusting the quantity of heat supplied.

The other parts of the apparatus, with the exception of the after-glow tube, were the same as those used in previous experiments. The spectrograph used was a quartz spectrograph of strong illumination made by C. A. Steinheil Söhne & Co., and the intensities of lines were measured with a Moll type of registering microphotometer.

The light-emissions from various parts of the after-glow tube, after passing through the quartz plate window of the a tube and quartz-fluorite achromatic lens, fall on the slit of the spectrograph. It is necessary here to measure the temperature of the vapour at various points of the tube, and a thermocouple of platinum and platinum-rhodium was put in at the points A, B, or C. Point A is 2 mm. below, B 2 mm. above, while C is 1 cm. above the nozzle. It was found that the temperatures of these points were not sensibly altered in spite of the flow of the activated or non-activated nitrogen gas, and it can be conceived that the temperature indicated is that of the vapour itself.

Experimental Results.

(1) *Sodium*.—By gradually heating the bulb with a small Bunsen flame and allowing the stream of the activated gas to flow continuously, a yellow glow begins to appear at the nozzle when the thermocouple indicates the temperatures 250° C. and 160° C. at A and B respectively. This glow gradually spreads out as the temperatures at A and B increase, and a greenish-yellow core appears at the stage when the temperature indication at B is 250° C. It should here be remarked that this greenish-yellow core is the intermediate stage leading on to the green core which is observed at the greater density of the vapour, and also that at this stage snow-like white compounds are deposited in a marked degree round the nozzle.

As shown in Pl. XVIII., *a* and the microphotogram (*e* in the same plate), the spectral lines observable from this yellow glow are lines belonging to the principal series; the D-lines are the strongest, the second member at λ 3302.03 Å. moderately intense, while the third member is so faint that it requires a very long time to photograph it. The lines of the subordinate series are weak.

Further, as the temperature of the bulb increases, a green core at the nozzle appears in the yellow diffused glow. One of the spectrograms obtained at this stage is reproduced

at *b* in the annexed plate, at which the temperatures at A, B, and C were 360° C., 260° C., and 240° C., respectively; spectrogram *c* was obtained at the stage when the temperature of the bulb was higher and the green core more extended in volume. As the yellow aureole always surrounds the central green core, it is impossible to observe the light from the central core alone by using type (*a*) as the after-glow tube, and we have used another type as shown in fig. 1 (*b*), the diameter of which is 1 cm. and that of the nozzle 5 mm. One example of the spectrograms from this central core is reproduced in Pl. XVIII., *d*. On comparing record *d* with *a*, we see that there are remarkable differences between them. Firstly: in the green core the first subordinate series is more enhanced than the principal series, while in the case of the yellow aureole this effect is reversed. Further, the intensities of the lines of the former series are greater than those of the energy corresponding member lines of the latter series; and as the levels of energy become higher and higher, this fact becomes more and more conspicuous; *i.e.*, the lines of the first subordinate series come out clearly up to higher levels than those of the principal series on the photographic plate. Also, the lines of the second subordinate series appear up to the higher terms in the green core. The microphotometric study of the spectrogram also confirms this conclusion (Pl. XVIII., *f*). Secondly: in the green core the second member of the principal series is more intensely developed than the first member in the plate, and the third member appears moderately intense; in other words, on the plate the intensity maximum is displaced towards the higher member, while in the yellow aureole the intensities of the lines of this series decrease rapidly with the term number of the series. Thirdly: in the green core the green band spectrum is visually observable in the position lying between the lines $2p-4d$ and $2p-6d$. These bands are due beyond any question to the sodium molecules Na_2 , though the red bands accompanying these green-blue bands are so faint that we failed to observe them. As is remarked in a later paragraph, an indigo-coloured new band system comes into view in the more dense vapour state of the green core. Lastly, it will be worth remarking that the deposit formed near the nozzle is dark grey in colour, and the amount of it is not so great as in the case of the yellow core.

The lines recorded in both plates after 5 hours' exposure, one observed through the yellow aureole and the other through the green core, are given in the following table. Under both conditions the lines of the higher members can

also be observable on the plate with an exposure of many hours' duration :—

Obs. Lines.			
Yellow Aureole.	Green Core.	Class.	Energy.
5890-96	5890-96	1s-2p	2.09
3302-03	3302-03	1s-3p	3.74
	2853	1s-4p	4.23
	6161-54 to	2p-3s to	4.09 to
	4423-20	2p-7s	4.88
5688-83	5688-83 to	2p-4d to	4.26 to
	4216-13	2p-12d	5.02

(2) *Potassium*.—Similar phenomena were observed in the case of potassium and cæsium. In the case of potassium vapour, the outer diffused aureole is faint green and the dense central core is pink. In the outer aureole the principal series, 1s-3p and 1s-4p, appears intense and the subordinate series lines are weak. On the other hand, in the pink core the subordinate series is more enhanced than in the case of the outer aureole. It is also noticeable that similarly as in the case of sodium, the lines at λ 3217-18 Å. and the higher lines of the principal series are relatively enhanced in the pink core.

(3) *Cæsium*.—Through the purple aureole we observed the lines belonging to the principal series, while those of the subordinate series were very faint, and in the yellowish-purple core the lines of the subordinate series were more enhanced than in the case of the outer aureole. Also, the relative enhancement of the higher members of the principal series, for example, λ 3612 Å. and λ 3477 Å., were observed in the central core, in which the decrease of intensity in the subordinate series lines with the term number is much smaller than in the case of the principal series, similarly to the former two cases. As regards the absence of the lines observed in the cæsium and recorded in the previous communication, they are given in the following table :—

Obs. Lines.	Class.	Obs. Lines.	Class.
4555	1s-3p ₁	6973	2p ₁ -5d ₁
4593	1s-3p ₂	6723	2p ₂ -5d ₂
3876	1s-4p ₁	6213	2p ₁ -6d ₁
3889	1s-4p ₂	6010	2p ₂ -6d ₂
3612	1s-5p ₁	5845	2p ₁ -7d ₁
3477	1s-6p ₁	5664	2p ₂ -7d ₂
		5635	2p ₁ -8d ₁
6587	2p ₁ -4s	5466	2p ₂ -8d ₂
6355	2p ₂ -4s		

(4) *The Band Spectrum*.—As we have already remarked, when the pressure of the sodium vapour near the nozzle is

sufficiently high, a band spectrum is observed in the central green core, as shown in Pl. XVIII., *b*, *c*, & *d*, and also in the microphotogram (*f*, in the same plate). Two bands are observed which have maxima of intensity at $\lambda 4530$ and $\lambda 4364 \text{ \AA.}$; the latter is more intense than the former, and they may probably be identified with the bands at $\lambda 4541 \rightarrow 4498 \text{ \AA.}$ and $\lambda 4390 \rightarrow 4340 \text{ \AA.}$, which R. W. Wood and R. H. Galt* have observed in the fluorescence spectra of the sodium vapour excited by cathode rays. It must be borne in mind that in their experiment a small quantity of air was mixed in the vapour as impurity.

Owing to the small dispersive power of our instrument, it was impossible to observe precisely the structure of the band, and so any definite conclusions deduced regarding the origin of the bands may be inadequate. But certainly it cannot be due to the sodium vapour itself, as no one has hitherto observed the bands in wave-lengths in these positions in any spectrogram of pure sodium vapour; so they will probably be due to the molecules of sodium nitride, and a further investigation of the structure and the origin of these bands is desirable.

Interpretation of the Results.

The intensity of a spectral line depends mainly on two factors: (1) the concentration of the initial energy level of the atom; (2) the probability of the transition. The first factor depends on the external circumstances, but the probability of the transition is affected by these circumstances to a very small extent, and it may be regarded as the true atomic reality. The experimental results just described, regarding the intensity difference between the spectral lines in the yellow aureole and in the green core, in the case of sodium vapour, can be accounted for by taking into account the collisions of the second kind between excited atoms and neutral ones, and also the conclusions which were deduced by H. Bartels† from his experiments on the vacuum arc in sodium vapour; *i.e.*, the transitions allowed by the selection principle of the azimuthal quantum number are highly favoured in the excitation process by electronic collision. As the results are very clearly observable in the case of sodium, it is convenient to discuss the question in relation to this case, and apply our conclusions similarly to the cases of potassium and caesium vapours.

* R. W. Wood and R. H. Galt, *Astrophys. Journ.* xxxiii. p. 72 (1911).

† H. Bartels, *Zeits. f. Phys.* xxv. p. 378 (1924).

From the experimental result that, in the yellow aureole, the higher member lines in the principal series are much weaker than the lower member lines in comparison with the corresponding result in the usual cases of excitation, while the lines of the subordinate series are very faint, it will be conceived that the concentration of atoms to the states of lower levels is much greater than that to those of higher levels of energy, in comparison with that in the usual cases of excitation. As the energy available is sufficient to excite the higher levels, this interesting distinction is due entirely to the characteristic of the triple collisions. In the aureole, where the density of the sodium vapour is comparatively small, the electrons of the sodium atoms are initially in the $1s$ -levels, and are excited to the p -levels by receiving the energy from the activated gas, the line emissions of the principal series being thus caused.

In contrast with the case of the yellow aureole, the subordinate series in the green core is much more enhanced than the principal series, and there is another peculiarity, viz. that the second member of the principal series is more brightly developed than the first member, while the third member is also enhanced. It is to be considered that in this green core the sodium atoms are in the excited states of the $2p$ -levels, and the electrons are lifted to the higher levels by receiving energy from the activated gas, the line emissions corresponding to greater energy of excitation being thus caused. The reason why the considerable part of the sodium atoms in the green core is in the states of the $2p$ -levels may be explained if we consider the process of the collision of the second kind. Obviously, the electrons, at first, are excited to the $2p$ -levels as in the case of the yellow aureole, and there will be three possible causes of the concentration of the atoms in these excited states: namely (1) through the unexcited atoms absorbing the energy of the D-radiation, (2) through the activated gas colliding with many sodium atoms and exciting them to these levels, (3) through the exciting atoms colliding with other unexcited atoms, and, the energy being transferred from one to the other, the energy being reserved in the sodium atoms for a comparatively long duration. But there is no reason why the first and the second processes should be more favoured in the core than in the aureole, while the third process is much the more likely one in virtue of the greater density of the atoms in the core, and there must be many chances of radiationless transferences of energy occurring among the sodium atoms. And therefore the large concentration of the excited atoms

in the states of $2p$ -levels is certainly due to the collisions of the second kind. The weak appearances of the D-lines will also be explained as the consequence of conserving the $2p$ -levels in the atoms.

The second excitation process to the higher levels from the $2p$ -levels is to be considered as entirely due to the direct collision between the activated gas and the excited atom. It is clear that atoms present in the states of the $2p$ -levels are no longer in a condition to absorb the D-radiation, and, assuming a collision between two atoms in the states of the $2p$ -levels, it is difficult to explain the line emissions corresponding to a higher excitation energy than 4.18 volts. We must therefore conclude that the energy-lifting of the electron to the higher levels comes directly from the active nitrogen.

As the greater part of the atoms is lifted to states of higher levels from the $2p$ -levels upwards, the enhancement of the subordinate series is clearly conceivable in the core, and the energy by which the electron is excited to the higher p -levels from the normal level is greater than that by which it is excited to the s - or d -levels of the energy corresponding member lines from the $2p$ -levels upwards; it therefore follows that the higher terms of the subordinate series are more enhanced under these circumstances than those of the principal series. In this case the secondary transitions to the $3p$ -levels from the higher s - or d -levels occur in addition to the primary transitions to the $3p$ -levels from the $1s$ -level, and we can understand why the second member of the principal series appears brightly. It may also be considered that the line emissions of the higher members of the latter series are mainly due to these secondary transitions.

As described above, all the results obtained in this experiment can be satisfactorily explained by taking into account the effects of the collisions of the second kind and that of the azimuthal selection principle in the excitation process by the active nitrogen. The phenomena described in this communication can only be observed in the case of the alkali metals, but not in the case of other metals.

In conclusion, the present writers express their best thanks to the Saito Gratitude Foundation for the expenses of this experiment, which were paid by the Research Fund from the Foundation.

Sendai, Japan.
October 1928.

LXXXVII. *Note on Superposed X-Radiations. J-Phenomenon* (Part IX.). By C. G. BARKLA, F.R.S., and M. M. SEN GUPTA, Ph.D., University of Edinburgh*.

IT was shown by Barkla and Miss Mackenzie that the superposition of a beam of Röntgen Radiation (Y) on another beam (X) changed the properties of that beam X; that X and Y proceeding together from neighbouring sources behaved, as far as the J-Phenomenon was concerned, as a radiation with properties of its own distinct from that of X or Y; that the J-discontinuity for the beam $X + Y$ was in the position not appropriate to either of the constituent beams X or Y, but in a position between these and appropriate to the radiation $X + Y$ as a whole.

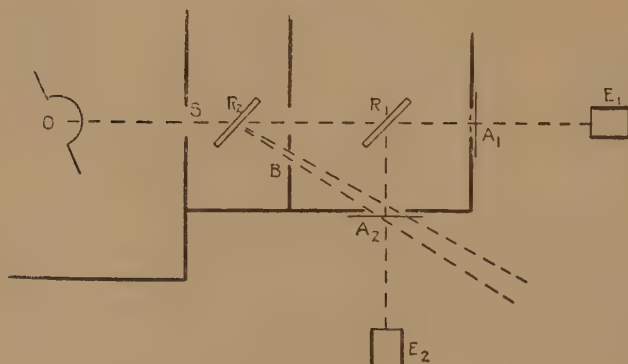
In the experiments referred to above, the two radiations X and Y were radiations scattered from neighbouring scattering plates, they were propagated together in the same direction, through the same absorbing sheets into the same testing ionization chamber. The feature which was observed was the J-discontinuity in the absorption in aluminium as an increasing thickness was placed in the path of the radiation to the ionization chamber. The critical thickness of aluminium at which the discontinuity occurred was equally dependent upon the original and the superposed radiations—indeed each constituent radiation made only its contribution to some kind of average, analogous to temperature, which controlled the phenomenon. It was this property of “coherence” of superposed X-radiations which we decided to investigate further, and to study under even simpler conditions than previously. For, as stated, the beam Y was superposed on the original beam X from its source, through the intervening air and the absorbing aluminium, and finally across the ionization chamber used to measure the intensity. Though other experiments had shown that the critical state was produced in the absorbing sheets of aluminium, for the discontinuity was characteristic of that substance, it seemed advisable to limit the superposition to that produced in the absorbing substance alone, and, in particular, to avoid superposition in the ionization vessel. In the experiments described below, therefore, the two superposed beams X and Y had their origin in two widely separated scatterers; they proceeded in directions making an angle of approximately 45° with one another; they crossed the absorbing sheets and separated again so that the ionization produced by the beam

* Communicated by the Authors.

X was studied quite independently of that produced by the beam Y. Superposition thus occurred only in and immediately around the absorbing aluminium. As will be seen below, the two beams were still "coherent"; the transmission of the beam Y through the absorbing aluminium affected the absorption of the beam X.

Preliminary experiments were made under conditions very similar to those of the experiments of Barkla and Miss Mackenzie. In our experiments, however, the scattering substance was paraffin-wax or paper instead of aluminium, and the scattered radiation studied was that proceeding in a direction approximately at right angles to that of propagation of the primary radiation. The discontinuities again occurred in positions appropriate to the beam

Fig. 1.



as a whole, and were displaced by the superposition of other radiations. The results agreed in all essential features with those of Barkla and Miss Mackenzie.

Experimental Arrangements.

The simplifications of conditions which we proposed was effected in the following way :—

The arrangement of apparatus is shown in figs. 1 and 2 in which most of the lines represent lead screens. Slabs of paraffin-wax were placed in positions R_1 and R_2 , so that when the lead shutter at the aperture S was removed, they were both exposed to the primary radiation from the Coolidge Tube O. In one case (fig. 1), R_2 was traversed by the primary radiation before its incidence on R_1 . In the other case, R_2 was exposed to the primary radiation after transmission through the radiation R_1 . Thus in the

former case, the heterogeneous radiation scattered from R_2 was on the average "softer" than that from R_1 ; whereas in the other case the radiation from R_2 was "harder" than that from R_1 . Apertures in the lead screens permitted the secondary radiations from R_1 to pass directly into the ionization chamber E_2 , and that from the radiator R_2 to cross its path by means of the aperture B. Consequently, it was necessary only to remove a lead screen from aperture B in order to superpose the radiation from R_2 on that from R_1 as it traversed the absorbing sheets at A_2 . Thus the absorption of the radiation from R_1 was compared under the two conditions—(1) without and (2) with the radiation from R_2 passing through the absorbing sheets. The method of procedure was to observe the ratio of ionizations produced by the secondary and primary radiations in the ionization chambers E_2 and E_1 . Let this ratio be S/P . Similar sheets of aluminium were placed across the apertures A_1 and A_2 , and the ratio S'/P' of ionizations produced by the transmitted radiations was again determined. As this was done for increasing thicknesses of aluminium, the ratio S'/P' suddenly dropped, when the critical condition for the scattered radiation was reached. When, however, the scattered radiation from R_2 was allowed to cross the absorbing aluminium, the discontinuity in the absorption of the radiation from R_1 occurred at a different point, that is, for a different thickness of the absorbing sheets. Also the displacement of the discontinuity was invariably in that direction which was found when the superposed beam was a constituent part of the radiation, the absorption of which was being tested. Thus with the arrangement of radiators shown in fig. 1, when the radiation from R_2 was prevented from falling on the absorbing aluminium at A_2 the J-discontinuity in the absorption of the radiation from R_1 occurred for a thickness of aluminium between $\cdot 03$ and $\cdot 04$ cm. Whereas, when the absorber was traversed by the radiation from R_2 the discontinuity in the absorption of the R_1 radiation occurred at a thickness between $\cdot 05$ and $\cdot 06$ cm. (See fig. 3, experiment 1.) In this case the superposed radiation (from R_2) was "softer" than the radiation experimented upon, consequently the whole atmosphere of radiation in the absorbing substance was "softer" than when the absorbed radiation was alone. The absorbed radiation had thus to traverse a greater thickness of absorbing aluminium before the average absorbability reached the critical value.

With the other arrangement of radiators, shown in fig. 2, the superposed radiation from R_2 was of more penetrating

type than that of the radiation from R_1 ; consequently, the superposition of the R_2 radiation made the whole atmosphere of the radiation traversing the absorbing aluminium, on the average, of more penetrating type. Hence, a smaller thickness of absorbing aluminium was necessary to bring the average absorbability to the critical point. In this case,

Fig. 2.

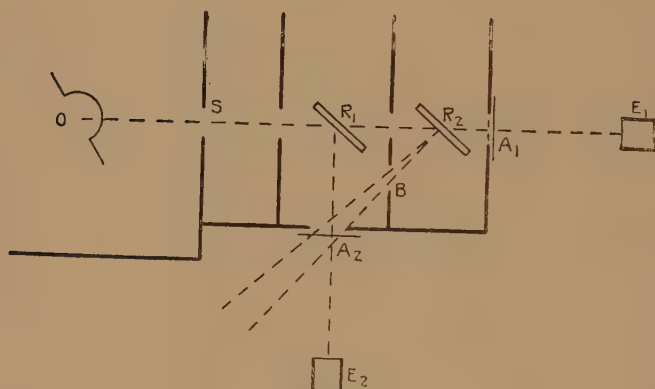
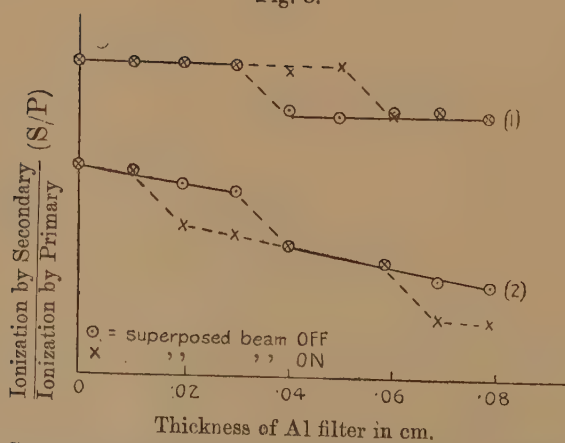


Fig. 3.



Case 1 = superposed radiation of lower average frequency.

Case 2 = " " of higher " "

Showing displacement of J-discontinuity by a second radiation.

then, the superposition of the R_2 radiation displaced the J-absorption discontinuity in the reverse direction, *i. e.* to the left of fig. 3.

These results are exhibited graphically in fig. 3, Exper. 2. The horizontality of the lines in fig. 3, Exper. 1, illustrates again the equal absorptions of scattered and primary radiations away from the discontinuity. The gradient in Exper. 2 indicates, of course, greater absorption of the scattered radiation, as was to be expected when the scattered radiation studied was that from the *front* face of the scattering sheet. This was of no significance in our experiments; the position of the discontinuity was the feature under observation, and this was as clearly marked in one case as in the other.

It is important to notice that, except for the discontinuity, the absorption of the scattered radiation was precisely the same whether the radiation from R_2 was "on" or "off," *i. e.*, the absorption of the radiation from R_1 was not affected by the superposed radiation. This is shown by the positions of the circles and crosses away from the discontinuity; they are superposed in fig. 3.

The question naturally arises, does the discontinuity—that is the sudden diminution in ionization*—indicate true absorption? To give all the evidence on the subject would require a separate paper, but sufficient has already been indicated in previous communications. It is the sudden occurrence of a process which, under other conditions, may be made more gradual and which is then generally recognized as absorption—indeed, it cannot be anything but absorption as the term is generally understood.

Thus the absorption of a given radiation, when the condition is neighbouring on a J-discontinuity, is dependent on other radiations traversing the absorbing substance. In other words, the absorbing property of aluminium (and presumably of other substances) depends not merely upon the radiation, the absorption of which is being measured, but upon the whole atmosphere of radiation traversing that absorbing substance. And thus again we have shown that the processes taking place in matter traversed by radiation depend upon a "coherence" of the various constituents of that radiation—a coherence, that is, in the sense that the constituents *combine* to produce an absorbing state in the matter itself. As far as we have seen, every constituent in the radiation affects the absorption of the other constituents; the radiation must be considered as a whole and not as a number of independent parts. To what extent, either in space or time, this coherence is effective is a matter for further experiment. It will be interesting to determine

* The "step" was about 7·5 per cent. of the total ionization measured.

whether such a coherence can be established between the radiations from two entirely independent sources. In our experiments the two radiations superposed must necessarily have been very similar in structure, for they were the radiations scattered from the same primary beam in transmission through substances of the same constitution. Whether or not the radiations scattered by (a) *dissimilar* substances from the *same* primary beam, or (b) *similar* substances in *different* primary beams, or even by (c) two *similar* substances in the *same* primary radiation, but widely separated so as to produce a very large difference of path, would have "cohered" it is impossible to say without further investigation. Such experiments as have been made by superposing γ -rays upon X-rays have indicated the complete independence of the two; but we are not yet prepared to say that coherence does not occur under favourable conditions. For the present, the intimate relation between two radiations traversing matter at the same time is the important thing; indicating, as it does, that all the constituents in the atmosphere of radiation are contributing to the state of the matter which controls absorption—at least that portion of it which we have called the J-absorption.

LXXXVIII. *Chromium Echelette Gratings on Optical Flats for Infra-red Investigations.* By R. W. WOOD*.

[Plate XIX.]

ECHLETTE gratings were first described in the Phil. Mag. for Oct. 1910. They were ruled with an hexagonal carborundum crystal, mounted, as shown by a figure illustrating the paper, on plates of polished copper as supplied for the half-tone process of photo-engraving. The surfaces of these plates had a very poor "figure," of course, and the gratings could not be used for precision work. In spite of this, however, the author, in collaboration with Professor A. Trowbridge (Phil. Mag. Nov. 1910), resolved the CO_2 band into a doublet with maxima at 4.3μ and 4.43μ . This was two years before Bjerrum predicted the doublet structure of vibration-rotation bands (also foreseen by Lord Rayleigh as long ago as 1892), the experimental verification of the theory being usually attributed to Burmeister (*Ver. deut. phys. Ges.* xv.

* Communicated by the Author.

p. 589, 1913) and Eva v. Bahr (for CO) (*Ver. deut. phys. Ges.* xv. p. 710). As a matter of fact, the experimental proof of the Rayleigh-Bjerrum theory was already accomplished two years before the appearance of Bjerrum's paper. The theoretical importance of the observation was, of course, not realized at the time, and the paper was published under the title "Notes on Infra-red Investigations with the Echelette Grating." It is therefore not surprising that the matter was overlooked.

The recent increase in the field of research in infra-red spectroscopy, resulting from the development of the theory of molecular band spectra, has made it appear worth while to improve this type of grating. As is well known, very excellent results have already been obtained with echelettes ruled on aluminium at the University of Michigan.

It was found that carborundum crystals were too fragile to be depended upon, but excellent results were obtained, with a diamond ground and polished to the proper angle, on optical flats of copper plated with gold. The Hilger Company furnished the plates with which the first of the new experiments were made, and some very fine echelettes were ruled on the old Rowland engine. A photograph of one of these with 2060 lines to the inch is reproduced (Pl. XIX.) standing upright on its printed label. It throws nearly all of the energy into the eighth order for mercury green light, and the reflexion of the printed characters on the label appears in an oblique direction (in the ruled portion) in the spectrum of this order. This grating would give a first-order spectrum in the same direction for radiations of wave-length $4.3\ \mu$.

It seems probable, however, that the gilded gratings may not prove very durable in the presence of mercury vapour, and experiments were accordingly undertaken to see whether a surface of chromium could be used. The gold gratings were plated before the ruling, as with a properly-mounted diamond no metal is removed during the ruling, the grooves being pressed into the material. This method could not be employed in the case of chromium plating, owing to the excessive wear of the diamond on the very hard metal. It was found, however, that the chromium could be deposited electrolytically, after the ruling had been accomplished, without changing in the slightest degree the distribution of the light. Gratings of this description on disks of copper 4 inches in diameter and $\frac{3}{4}$ of an inch in thickness can now be supplied to any laboratories desiring them. They can be ruled for concentration at any desired wave-length range

(expressed in μ) and with any desired spacing, though we choose the spacing according to the region to be investigated.

Some very good concave echelettes of 1 and 2 metres radius have also been made which resolved the CO_2 band easily, but it is believed that plane gratings will prove more satisfactory, as they can be used with long-focus mirrors for high resolution and with short-focus ones for intensity. A collection of three or four, ruled for concentration in different spectral regions, is desirable. The 4-inch gratings are priced at \$100 each.

The ruling of 5-inch disks will be commenced very shortly.

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LXXXIX. *The Raman Effect in Gases.*—Part I. *HCl*
and *NH₃*. By R. W. WOOD*.

[Plate XX.]

AS mentioned in a letter to 'Nature' of Feb. 2, spectrograms have been obtained of the lines of modified wave-length in the light of the mercury arc scattered by a gas at atmospheric pressure. A very special technique is required, on account of the weakness of the light; nevertheless, records have been secured with an exposure of only five hours with an F 2 one-prism spectrograph, by employing the apparatus to be described presently. With HCl a very surprising result was obtained, namely: for each exciting line a single line only, of modified wave-length, was radiated, and the frequency difference between the exciting and emitted radiation was the frequency of the "missing line" of the infra-red absorption band at 3.4645μ . The spectrogram from which this determination was made was a Bausch and Lomb constant deviation spectroscope, the camera lens having a focus of 50 cm.

The three prime requisites for obtaining the effect with gases at atmospheric pressure are: very intense illumination of a long column of gas, an absolutely black background, and complete absence of scattered light from the front window. The last condition is the most important and the most difficult to fulfil.

The apparatus employed is shown in fig. 1. It consists of a tube of soft glass 5 cm. in diameter and about 150 cm. in length, drawn off into a tapering cone at the rear, and constricted and expanded at the front as shown in the diagram.

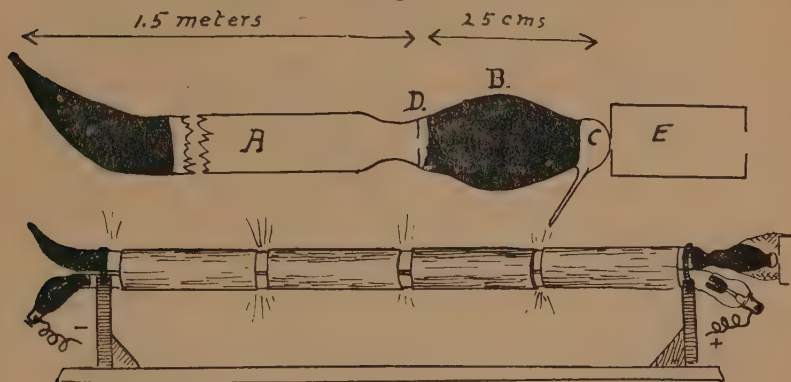
* Communicated by the Author.

The lower figure is drawn more nearly to scale, and shows the tube mounted over, and in contact with, a very long Cooper-Hewitt mercury arc lamp of glass. Hollow cylindrical reflectors of very thin highly polished sheet aluminium enclose the two tubes, shutting in all of the light. This is a great improvement on the earlier "light furnaces" described in former papers on iodine fluorescence.

The cylinders were made by wrapping rectangular sheets of the metal around a glass tube of much smaller diameter than that desired, a size being chosen such that the edges of the sheet remained in contact when it expanded by its elasticity.

The cylinders are slipped over the tubes by springing them open with the fingers, and on releasing them they

Fig. 1.

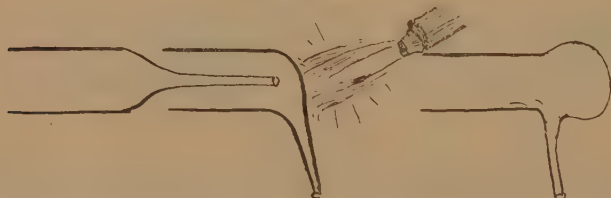


clamp themselves firmly around the two tubes. The upper diagram is not drawn to scale. The bulb B is rather longer in proportion to its diameter than is indicated in the figure. This bulb prevents reflexion of light coming from the mirrors and lamp through the diaphragm D, against the front wall of the bulb C. The preparation of this latter bulb is the most important part of the whole operation. It must be as thin as possible and optically clean, *i. e.*, free from air-bubbles, striæ, or cloudiness. The front wall should not be thicker than thin writing-paper, and if properly made gives almost as clear vision down the tube as a plate-glass window. A window of thin cover glass could be cemented on, in the case of most gases, but I preferred the bulb for the work with HCl.

The diaphragm D is a disk of very thin platinum foil, perforated by a hole 4 mm. in diameter, which is as large

as can be safely used, as the condition which must be fulfilled is that *no part* of the lens used for projecting an image of diaphragm on the slit, can "see" any part of the blazing interior of the furnace through the diaphragm. The platinum disk is dropped into position resting against the sloping wall of the constriction (the tube being held vertically), and the glass then melted in spots with a small pointed blast-lamp flame until it takes hold of the platinum. The bulb B is then blown, drawing it out during the blowing, and finally the end bulb and exit tube prepared. The three stages of this process are shown in fig. 2. The tube is first drawn down, and bent at a sharp right angle as shown, the narrow tube being about 20 cm. long, however, so that it can be used for blowing the bulb. The flame is then directed against the flattened end and the bulb blown to paper thickness. It is wise to practise blowing these thin bulbs on some scrap pieces of tubing of the same size, before

Fig. 2.



making the long tube. The tapering cone and the large bulb are now painted black on the outside. "Duco" auto-enamel paint will answer, but an asphaltum paint is slightly blacker and preferable for the cone.

E is a cardboard mailing cylinder covered with black paper at each end perforated with small holes as shown. This is to screen the front surface of the bulb from light from the walls of the room and neighbouring objects. After mounting it in place, a piece of black cloth is wrapped around the bulb and cylinder as shown in the lower figure. This prevents light escaping from the end of the "furnace" from reaching the black paper and being in turn reflected against the front bulb wall. The room is dark except for the light which escapes from the furnace.

The tube was filled with dry HCl , the gas being introduced through the cone end, with the tube in a vertical position, and the exit tube close to an open window with an outward draught. Small samples of the escaping air were taken in a test-tube from time to time to determine when the gas had

reached the top. The ends of the tube were then sealed with a flame. Notwithstanding the circumstance that the tube had been heated and ventilated with dry air for some time previous to filling it with gas passed over calcium chloride and phosphorus pentoxide, it showed a marked "fog" when illuminated in the furnace. After standing overnight, however, it cleared up and gave no further trouble. The gas was prepared by dropping concentrated sulphuric acid into a flask containing hydrochloric acid, through a funnel tube which dipped below the surface of the acid. The sulphuric acid was fed into the funnel at the rate of about one small drop every three seconds by means of a second funnel drawn down to a capillary.

The Cooper-Hewitt lamp was mounted on two thin wooden supports in V-shaped notches lined with asbestos board, and the gas-tube held down in contact with it by thin metal bands screwed to the supports and passing over the tubes.

The illumination produced in this way is terrific as the light of the lamp is beaten back and forth between the walls of the reflectors, and, as I have said, it was possible to photograph the modified line with a five-hour exposure, while the unmodified line comes out with an exposure of only 15 seconds, some of the light in this case coming undoubtedly from the "black cone" and the front wall of the bulb.

The proper aiming of the spectrograph is very important, a matter concerning which too little has been written. In the present case the best method is the following. We bring the eye in line with the two holes in the pasteboard cylinder, at a distance of about 1.5 metres from the end of the cylinder, and find the point from which we view the centre of the black cone at the far end of the tube through the platinum diaphragm. The edge of the circular aperture appears as a bright ring of light by diffraction. We now mark the position of the pupil of the eye by means of a match-stick held in a clamp stand, and moving the eye up and down and to the right and left, make sure that no direct light from the furnace walls will reach the lens which is to be mounted between the eye and the tube at a distance from the former equal to its focal length (with respect to the diaphragm).

The slit of the spectroscope is now brought up to the end of the match-stick, and the eye brought into the position to be occupied by the photographic plate. It may facilitate matters to place a "pea" electric lamp in front of the small hole in the black paper on the end of the cylinder. If the spot of light coming through the wide open slit is not at the

centre of the field, the spectroscope must be turned accordingly, keeping the slit in coincidence with the marker, however. An achromatic lens (I used an F 4.5 Zeiss photographic objective of about 25 cm. focus) is now mounted in such a position as to form a sharp image of the hole in the platinum diaphragm on the slit, the approximate position being found with the "pea" lamp. It is of vital importance that a sharp image is obtained, otherwise the light diffracted by the edge of the aperture will ruin everything, for the mercury arc has a fairly strong continuous background.

We assure ourselves of this by getting a sharp image of the jaws of the slit (using a short-focus magnifier), and the bright circle of diffracted light at the same time, viewing them without a ground glass focusing screen of course. It is assumed that the spectrograph is properly focussed. The projecting lens is to be moved forward or back until the appearance of the wide open slit, seen by the light of the green line, is as shown by fig. 2 (Pl. XX.), the two bright arcs being the upper and lower edges of the hole in the platinum disk shining by diffracted light while the luminosity between them comes from the gas.

Fig. 1 (Pl. XX.) shows the line of modified wave-length scattered by dry hydrochloric acid gas at atmospheric pressure. It falls nearly midway between the mercury lines 4358 and 4915 almost in coincidence with the argon line 4579.5, and its wave-length as determined from a plate made with higher dispersion than the one reproduced is 4581.8.

This line is excited by the mercury line 4046. The corresponding line excited by 4358 was recorded on one plate made with the F2 short-focus spectrograph, but it was very faint as it fell in a region of low sensitivity. The frequency difference between Hg 4046 and the HCl line corresponds to wave-length 3.466μ in the infra-red.

Now this is almost exactly the wave-length of the "missing line," or the centre of the gap between the two branches of the absorption band as resolved and measured by Imes. The Raman line in this case does not identify itself with an absorption line, but does identify itself with a Q branch (vibration without rotation change) not observed in absorption. Professor Kemble has calculated that the "missing line" should have a wave-length of 3.4649μ , and the Q branch 3.4689μ . My value of 3.466 is in very fair agreement with this calculation. I have not yet found an explanation for the circumstance that on my first plates I found two lines, as reported in 'Nature.' One of these was the line 4581.8 (which we have been discussing), and the

other was of slightly greater wave-length. The tube in this case contained a trace of water-vapour, and with a fresh filling with dry gas the single only has appeared. Experiments will be continued with this gas excited under varying conditions of temperature and with water-vapour, and other impurities, mixed with it. I hope to be able also to make still more accurate determinations of its mean wave-length and width, for it is distinctly wider than the argon comparison lines.

There are also a number of nearly equidistant bands close to the 4358 mercury line, which I at first thought might be interference maxima due to the passage of the light of the faint continuous spectrum through the very thin wall of the glass bulb, but I am now not sure but what they are real. If excited by the 4358 line, they might be identified with the rotation bands found by Czerny (*Zeit.f. Phys.* xxxiv.) between 40 and 100 μ .

The infra-red wave-lengths corresponding to these bands were calculated and found to agree fairly well with the *alternate* lines found in absorption by Czerny, as follows:—

Czerny.	Wood.
44.1	43.6;
48.5	—
53.8	53.9
60.4	—
68.9	67.1
80.4	—
96	90 (Uncertain).

It is not worth while, however, to discuss them seriously until they have been obtained with a new tube having a bulb with a thicker wall.

Ammonia at atmospheric pressure gave a single line also, for each exciting line. A very sharp triplet excited by Hg 3650, 3654, and 3663, of which the outer lines had wave-lengths of 4157 and 4172. The 4046 line excited a line of wave-length 4672.5. Thus far I have photographed these with the F2 spectrograph only, and the wave-lengths are not very accurate. These lines are identified with the infra-red absorption band at 3 μ .

The ammonia was taken from a commercial iron cylinder and not purified. Coblenz gives this band at 3 μ and it is Band II. of Sir Robert Robertson's recent paper (*Proc. R. S.* 784, p. 161). No trace of lines corresponding to the strong ammonia bands at 6.5 μ and 10 μ have been observed as yet.

XC. *Notices respecting New Books.*

Beyond the Electron. By Sir J. J. THOMSON, O.M., F.R.S.
(Cambridge University Press. Price 2s. 6d. net.)

THE recent experiments of Prof. G. P. Thomson on the passage of cathode rays through thin films of metals have furnished a remarkable verification of the de Broglie theory of electron waves.

These researches form the starting-point of the lecture on the structure of the electron and its surroundings. The electron is accompanied by a train of waves of very high frequency; the theory, on the basis of "Classical Mechanics," is set out in a supplementary note and the author shows that, between the wave-length and velocity of the electron waves, the same relation holds as for light-waves in a superdispersive medium, that the energy of the electron is proportional to the frequency, and the product of momentum and wave-length is constant. The new fields of research opened up by the experiments of G. P. Thomson, Rupp and Davisson and his co-workers will throw further light on the structure and properties of the electron.

Theory and Application of Infinite Series. By Dr. KONRAD KNOPP. (Translated from the second German edition by Miss E. C. YOUNG, L. ès Sc.) (Blackie and Son, Ltd. Price 30s. net.)

THE translation of Prof. Knopp's 'Theorie und Anwendung der unendlichen Reihen' deserves the favourable reception accorded to the first and second German editions, and thanks are due to the publishers for placing this translation in the hands of English readers. Private students in particular will fully recognise the debt they owe to the author for his useful and comprehensive work.

The first two chapters deal with real numbers and sequences, followed by several sections on series of positive terms, power series, infinite products, and series of complex terms. The section on divergent series has been considerably extended and sets out much of the recent work on this subject. The chapter on Euler's summation formula and asymptotic expansions has been specially written for the English edition and gives a review of the work of Stieltjes on asymptotic series, particularly in their application to the calculation of functions, *e.g.*, the exponential integral with both positive and negative argument. The very large number of practical exercises form a valuable feature of the book.

The Spectroscopy of the Extreme Ultra-violet. By THEODORE LYMAN. (Second edition. Longmans, Green & Co. Price 10s. 6d. net.)

WHEN the first edition of this book appeared some fourteen years ago Prof. Lyman had investigated the Schumann region as far as λ 900, and, two or three years later, to λ 500. In this second edition the author has incorporated some of the notable results in the region of still smaller wave-lengths, in particular, Millikan's work with the hot spark, first described by R. W. Wood thirty years ago, bringing the limit near λ 140. From the region of the soft X-rays, Dauvillier and others have obtained radiations of wave-length near Millikan's limit, with the consequent removal of the gap between optical spectra and X-rays. In the chapter on Emission spectra, the author has made available a mass of information on the spectra of a large number of gases and solids in the extreme ultra-violet. In addition to the tables of wave-lengths of the spectra of hydrogen and other elements, there is a bibliography of papers which have mostly appeared since the publication of the first edition of Prof. Lyman's book.

The Discovery of the Rare Gases. By MORRIS W. TRAVERS, D.Sc., F.R.S. [Pp. vii + 128, with frontispiece and 21 figures.] (London: Edward Arnold & Co. 1928. Price 15s. net.)

PROF. TRAVERS, in the course of arranging, at the request of Lady Ramsay, the scientific papers of the late Sir William Ramsay, came across a complete series of laboratory notebooks. Many of these contained little more than numerical data with brief descriptive notes, but with the commencement of the work which led to the discovery of argon, experiments were described in detail and drawings of apparatus given.

The original intention of Prof. Travers was to annotate and summarize these for the benefit of the future historian of the chemistry of recent years. This project was expanded until a manuscript volume giving an account of the discovery of the rare gases had been prepared. Friends and colleagues to whom the manuscript was shown insisted that it should be published.

Based as it is upon Sir William Ramsay's own notebooks and written by one who assisted in a large portion of the investigations described, the accuracy of the account can be relied upon. The successive stages of the long series of investigations, the first-fruits of which were the discovery of argon, and which led to the discovery, in order, of helium, krypton, neon, and xenon, are recounted. There were many difficulties to be faced; not only the difficulties inherent in the research itself but also difficulties arising from lack of funds for the purchase of apparatus and difficulties in obtaining the liquid air and hydrogen required. Liquid hydrogen was finally obtained from an extemporised plant

constructed by Prof. Travers himself, and this enabled the investigations to be brought to a successful conclusion.

The two guiding principles to which Sir William Ramsay firmly adhered, in the face of much opposition, and which crowned these investigations with success, were: (i.) that a ratio of 1.67 for the specific heats of a gas is indication that the gas is monatomic; (ii.) the new gases had to fit in a proper manner into the periodic system of the classification of the elements.

The volume is illustrated with diagrams of apparatus and reproductions of pages from the original notebooks.

Old Mother Earth. By KIRTLEY F. MATHER. [Pp. xiv + 177, with 61 illustrations.] (Cambridge: Harvard University Press. London: Oxford University Press. 1928. Price 11s. 6d. net.)

DURING the winter of 1927-28, the author was asked to give a series of broadcast talks at Boston dealing with the past history of the Earth. These talks, somewhat modified, are published in the volume under review. The author deals with the origin of the Earth, the origin of life, the evolution of mankind, the great ice-age, the formation of coast lines, earthquakes, and the formation of mountains. He has the gift of popular exposition; technicalities are avoided, but not at the expense of accuracy. The volume can be recommended to all who wish to know something of how the Earth, as we know it at present, has come into being. The arguments are illustrated by means of various geological features of New England, and the volume is therefore of greater interest to an American than to an English reader. The illustrations are numerous and good.

Bibliography of Crystal Structure. By J. K. MORSE. [Pp. xix + 164.] (Chicago: University of Chicago Press. London: Cambridge University Press. 1928. Price 15s. net.)

THIS publication is issued by the Crystal Structure Laboratory of the University of Chicago, which was started in 1926. Part I. contains an account of the present work of the Laboratory, an outline of its development programme, and reprints of the papers on the crystal and molecular structure of organic and inorganic compounds which have been published from the Laboratory. The bibliography of crystal structure, including the related topics of atomic dimensions and molecular structure, forms the second part of the volume. The bibliography is arranged alphabetically by authors under each year from 1912 to 1927, and contains about 1800 entries, emphasizing the wide interest of this branch of research. The bibliography should prove of great value for purposes of reference.

XCI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 424.]

December 5th, 1928.—Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President, in the Chair.

THE following communication was read:—

‘The Erratic Rocks and the Age of the Southern Limit of Glaciation in the Oxford District.’ By Kenneth Stuart Sandford, M.A., D.Ph., F.G.S.

The Plateau Drift around Oxford contains rocks brought from long distances:—from Scandinavia, Scotland, East Anglia, the Midlands, and, most surprising of all, from Devon and Cornwall. Excepting smaller pebbles, much of the material is subangular and some of it glacially striated.

The Drift entered the district through the Cotswold escarpment by gaps which the northern tributaries of the Upper Thames occupy, and it is found on their sides to a height of more than 600 feet above sea-level. There is no evidence of glacial erosion of the district within the scarp, though a few patches of Drift are recognized as Boulder Clay. The Drift is the homologue of the thick Boulder Clay which is still preserved outside the scarp; it was introduced either by a ‘fluvio-glacial’ inundation or during submergence, and was spread over the surface to the height stated irrespective of the old topographic features.

It is not suggested that heavy glacier-ice was the vehicle in every instance: for example, the material from the South-West was most probably carried on detached shore-ice drifting up the Bristol Channel. It is the presence of this material in the district which lends support to the view that the Southern Midlands in particular were submerged to a considerable depth.

The material, however introduced, was ‘graded’¹ or redeposited in terraces up to 350 feet above the recent rivers, this process being subsequent to, and distinct from, the introduction of the Drift into the district.

The erratics are believed to have been assembled under glacial conditions, evidently over a long interval of time, early in the Pleistocene Period. The Drift is older than the 140-foot and 100-foot terraces of the Upper Thames Basin; the former contains early Chellean implements and the latter a Chellean fauna. It is believed to be younger than the Cromer Forest Bed, containing earliest Palæolithic implements and a late Pliocene fauna. It seems to be older than the ‘Preglacial’ beach of the Bristol

¹ The Rev. C. Overy, Abstracts Proc. Geol. Soc. No. 1095 (1923) p. 28.

Channel, since a Chellean fauna comparable with that of the 100-foot terrace of the Thames is found in caves associated with the beach, the Preglacial age of which is viewed with some suspicion on this and other evidence.

Within the district a threefold glacial sequence is now established. It is emphasized that the first, the subject of this paper, was the maximum glaciation of the Southern Midlands and of early Pleistocene age. During the other two the district was an ice-free land-area, between the glaciers of the Eastern Counties and of Wales, and it is suggested that the rocks from distant places, including the older centres of glaciation, no longer enjoyed the freedom of dispersal of the early episode. The Oxford district being ice-free during these later glacial episodes, the conditions which then prevailed are faithfully recorded in the contemporary fluvial deposits and surface-changes. In East Anglia and elsewhere the remains of the early glaciation have been destroyed, or nearly so; they may be incorporated in the younger Boulder Clays.

The chronological sequence, based on this and two earlier papers, is as follows¹:—

- | | |
|--|---------|
| I. Plateau Drift with erratic material, maximum of glacial conditions within the district. | Mindel. |
| Chellean implements and 'warm fauna,' 140- and 100-foot terraces. | M/R. |
| II. 40 to 50-foot terrace (Wolvercote)? and older Gravels of the 20-foot terrace (Summertown) with 'cold fauna' and older Acheulean implements. | Riss. |
| Period of aggradation: Younger Gravels of the Summertown Terrace, with marked 'warm fauna' and Upper Acheulean implements, followed by Gravels and Sands of the Wolvercote Channel with 'warm fauna', Upper Acheulean and Micoque implements. | R/W. |
| III. Silts and Clays, with Reindeer and Mousterian (?) implements, filling the Wolvercote Channel; disturbed by 'Warp Sands' and Trail, which descended over older terrace-gravels as the river re-excavated its bed and dug its buried channel. | Würm. |

December 19th, 1928.—Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President, in the Chair.

Dr. C. A. MATLEY gave a short account, illustrated by lantern-slides, of a visit to the crater of Papandajan (Java) on January 7th, 1925, at which date, and for some twelve months previously, it was under observation by Dr. N. J. M. Taverne, of the Dutch East Indies Mining Service. The crater was closed to the public owing to a recent fatality, and Dr. Matley expressed his indebtedness to the Director for special permission to visit it, and also to Dr. Taverne for acting as guide and for explaining his methods of vulcanological research.

¹ Q. J. G. S. vol. lxxx (1924) pp. 113 *et seqq.* & *ibid.* vol. lxxxi (1925) pp. 62 *et seqq.*

The crater and its wall had been mapped on the scale of 1 : 2000, with contours, and all the vents and fissures recorded. The temperatures of the fumaroles, solfataras, hot springs, and mud-holes were taken daily. A seismometer and a Milne seismograph had been installed, and another of improved type was about to be erected. A torsion-balance had been ordered, with the object of ascertaining changes of mass in the volcano and detecting movements of the magma. The problem of determining the stages leading to an eruption and, if possible, of predicting it, was therefore being attacked from three sides: namely, temperature, crustal movement, and movement of magma. In addition, the nature and quantity of the gaseous emanations, and the changes in them, were also being studied. The general conclusion drawn at the time of the visit was that the mass of lava was rising, but had not yet come directly into action, as the volcanic ash thrown out at recent eruptions consists of previously consolidated and propylitized material, and no new lava is present in it. The study of this volcano is of importance, as no fewer than 3000 lives were lost in the eruption of 1772.

Descriptions were given of the phenomena seen, including the destruction of part of a forest by a recent eruption of propylitized ash. A full account of the observations by Dr. Taverne will be found in 'Vulkanologische Berichte' vol. xxxiii. (1924) & vol. xlii. (1925), as also in 'Vulkanstudien op Java' 1926.

January 9th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President, in the Chair.

Prof. OWEN THOMAS JONES, M.A., D.Sc., F.R.S., F.G.S., delivered the following lecture (illustrated by lantern-slides) on the History of the Yellowstone Cañon (Yellowstone National Park) U.S.A.:—

The Yellowstone Cañon is one of the most striking features of the Yellowstone National Park, which has long been famous for its geysers and its Tertiary volcanic rocks.

The Park has an area of 3344 square miles, which is almost equal to the combined area of Lancashire and Cumberland.

After leaving Yellowstone Lake, the Yellowstone River flows northwards through the Hayden Valley with a very small gradient. Both around the lake and in the Hayden Valley there are remains of several post-Glacial lake-terraces. The river then drops over the Upper Fall (108 feet), and in a short distance over the Lower Fall (309 feet). The so-called 'Grand Cañon' begins here, and extends to Tower Falls about 20 miles away to the north, where the very narrow precipitous 'second Cañon' begins. At the lower end of this cañon the Yellowstone is joined by the Lamar River, which flows in a wide-open, flat-floored valley, of great size and mature aspect. Below the junction of the rivers the so-called 'third Cañon' commences, and continues downstream towards Gardiner.

A preliminary geological survey of the Park was made by Dr. F. V. Hayden, who had among his assistants the famous delineator of geological subjects, W. H. Holmes, who, besides being a skilled artist, possessed unusual ability as a geological observer. The account of the geology of the Park in Hayden's Final Report for the year 1878 was contributed by Holmes, and this is still the best account of the physical features of the Park. In later years the Park was surveyed in detail by a field unit of the U.S. Geological Survey, under Arnold Hague, and a folio of maps, together with a summary description of the geology, was published in 1896.

The igneous rocks were described by Iddings in Monograph 32, Part II. Reference is made in this Monograph to the account of the physiography of the Park by Hague in Monograph 32, Part I. It appears, however, that the manuscript of this Monograph was not completed when Hague died, and it was never published.

The lecturer was privileged last summer to be the guest of the Summer School of Geology & Natural Resources, which was organized and conducted by Prof. R. M. Field, of Princeton University. During the visit of the Summer School two years previously, Prof. Field had photographed with a cinematograph camera a part of the cañon below the Great Fall, and, when the film was exhibited, he observed cross-bedded sediments on the side of the cañon near the prominent pinnacle known as Red Rock. Last summer Prof. Field and the lecturer examined these sediments in the company of Mr. W. J. Johnson, of the Canadian Geological Survey, and Prof. W. A. Parks, of Toronto University, and they found about 187 feet of alternating blue silts, yellow sands, and conglomerates, with a calcareous and tufaceous cement. The silts could only have been deposited in quiet water, and resemble lacustrine deposits. Similar sediments were observed on this occasion within 50 feet of the bottom of the cañon and about 100 yards of the foot of the Great Fall, and also in the ravine between the two falls where they are capped by a conglomerate at a level of about 100 feet above the Upper Fall. These sediments show that, since the cañon was eroded, it has been dammed somewhere below this locality, and filled to the brim with sediments. It is the prevalent opinion among physiographers that the cañon is of post-Glacial date, and the conglomerate capping the sedimentary series between the falls has been interpreted (E. de Martonne) as one of the Yellowstone Lake terraces. The conglomerate is, however, pre-Glacial, and appears to have nothing to do with the lake-terraces. A study of the geological maps in the folio suggests that the cañon was dammed by great flows of lava, which moved up it from the direction of Gardiner, and reached both the 'Grand Cañon' and for many miles up the Lamar Valley. Some of these flows consist of trachytic rhyolite, but most of them consist of basalts which are now preserved as remnants on the flanks of the cañon, descending in places to within about 100 feet of its floor and rising in places to a height of nearly 8000 feet. As the top of the sedimentary series between the two falls stands

at about 7800 feet, it is obvious that the lava-flows would be capable of damming the cañon to the depth necessary to allow of the formation of the sediments. The evidence of the sections exposed in the walls of the 'Second Cañon' near Tower Falls clearly shows that, in that region, an older cañon lying to the east of the 'Second Cañon' had been filled by alternations of basalts and conglomerate, and the present 'Second Cañon' has been excavated to one side of the old blocked cañon.

A consideration of the profiles of the Yellowstone Cañon, the Lamar River, and their tributaries shows that traces of three cycles of erosion are preserved. In the Yellowstone system the first cycle is represented by the Hayden Valley, the second cycle by the 'Grand Cañon,' and the third cycle by the 'second' and 'third' cañons. The lava-flows were poured out on the floor of the valley while the third cycle of erosion was in progress. The 'Grand Cañon,' which belongs to the earlier or second cycle, has been eroded through the rhyolitic rocks of the Park. The basalts which followed on the third cycle are, therefore, obviously younger than the rhyolites. The conglomerate between two of the basalt-flows has yielded the remains of a Pliocene horse, and is presumably of Upper Pliocene age.

The lecturer considered that a very great interval of time intervened between the eruption of the rhyolites and the eruption of the basalts. In the folio, however, the rhyolites are regarded as being younger than the basalts and conglomerate, an interpretation which is quite inconsistent with the physiographical history of the cañon, and also with the direct evidence in the field. A perusal of Holmes's report shows that he had grasped nearly all the significant points in the geological history of the region, and there is no doubt that, given a little more time, he would have completely anticipated the results obtained by Prof. Field and the lecturer.

The general volcanic history of the Park appears, then, to have been as follows. A vast thickness of andesitic breccias was poured out, either in late Cretaceous or in early Eocene times, on a very uneven surface which consisted of rocks ranging from Pre-Cambrian to Cretaceous. A long period of erosion intervened, and the surface of the andesitic breccias was dissected into a system of mature or sub-mature valleys. On to this surface the rhyolites were poured out. There is reason to believe that the surface of the rhyolites themselves had been peneplaned, and several hundreds of feet of the upper part of the rhyolites had been removed, before the initiation of the 'Grand Cañon' cycle, which was presumably the result of uplift. A further rejuvenation initiated the third cycle of erosion, represented mainly by the 'third' cañon, after which the basalts and trachytic rhyolites were erupted, leading to the damming of the 'Grand Cañon' and the deposition of the sediments near the falls. Since that presumed Upper Pliocene period, the basalts have been almost completely removed to a depth in places of nearly 1500 feet, the sediments

in the 'Grand Cañon' have been almost cleared out, and the erosion of the cañon, which had been arrested for an enormous period of time, has been resumed.

Two facts are very significant in connexion with the history of the region. One is the very large amount of material that has been removed from the whole length of the cañon since Upper Pliocene times, and the other is that the Great Fall of the Yellowstone has probably remained in its present position for an enormous period of time, and may perhaps be regarded as the oldest fall in the world.

January 23rd, 1929.--Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President, in the Chair.

The following communications were read:—

1. 'The South Wales End-Moraine.' By Prof. John Kaye Charlesworth, D.Sc., Ph.D., M.R.I.A., F.G.S.

The Irish-Sea Ice stood over Cardigan Bay at the period of the maximum advance of the Newer Drift period, and ponded back the natural drainage of Northern Pembrokeshire and Southern Cardiganshire to form a chain of extra-glacial lakes connected by marginal streams. This drainage, except at an early stage, failed to escape across the main watershed into the Bristol Channel, and was led along the ice-edge into Cardigan Bay. The largest lake occupied the valley of the Teifi, and was 34 miles long.

The end-moraine of the Newer Drift passes across Eastern and Southern Wales. In Northern Pembrokeshire and Southern Cardiganshire, where the moraine is rarely conspicuous and often absent over considerable stretches, it was laid down along the edge of the Irish-Sea Ice, contemporaneously with the operation of the highest marginal channels of these areas.

Farther east, the moraine is practically continuous, and represents the marginal product of the local Welsh Ice, which was centred in the mountains of Central Wales, the Carmarthenshire Vans, the Brecon Beacons, the Black Mountains, and the mountains of Radnor Forest. This ice flowed beyond the outlets of the great valleys of the east to form the valley-glaciers of the Severn, Cwm Lugg, Arrow, Wye, and Usk, and extended southwards on to the coastal plain of Glamorgan as the Glamorgan Piedmont Glacier and the Swansea Bay Piedmont Glacier. The end-moraine is disposed in loops around these glaciers, and passes beneath or near the following places: Tregaron, Swansea, Kyle, Cowbridge, Cardiff, Risca, Usk, Abergavenny, Pandy, Hereford, Wellington, Leominster, Craven Arms, and Montgomery.

This Newer Drift, which probably marks the culmination of the cold of the Glacial Period in Britain, is shown to be of early Magdalenian age by the collective evidence of the Upper Palæolithic implements of Britain. It was preceded by the 'Aurignacean

Oscillation', the minimum extent of which can be estimated from the distribution of the remains of the Pleistocene mammalia in the drifts and caves of the North of England.

The raised beach of the southern part of the British Isles is earlier than the Older Drift.

2. 'The Glacial Geology of the Derbyshire Dome and the Western Slopes of the Southern Pennines.' By Albert Jowett, D.Sc., F.G.S., and Prof. John Kaye Charlesworth, D.Sc., Ph.D., M.R.I.A., F.G.S.

The Derbyshire Dome of the Southern Pennines was overridden at the period of maximum glaciation by ice from the north and north-west. This is shown by the occurrence of fairly extensive patches of true Boulder Clay, ranging up to 20 feet in thickness, by the wide distribution of erratics of Lake District and Galloway rocks over the dome and along its valleys, and by a southward carry of the local rocks, such as Carboniferous Limestone (dolomitic and non-dolomitic, cherty and non-cherty varieties), Millstone Grit, and Toadstone.

The upper limit of the Galloway and Lake District erratics follows the outer flanks of the South-Western Pennines at an average height of about 1250 feet above sea-level, decreasing slightly southwards in the direction of flow.

The ice-recession from this position was associated with a copious marginal drainage, which eroded a well-developed suite of channels linking a number of big extra-glacial lakes in the valleys of the Western Pennines. These waters escaped at the same successive stages: (1) by the Walsden Gorge into the Todmorden valley and the Humber drainage; (2) by Dove Holes into the Wye, Derwent, and Trent basins; (3) into the Trent drainage by its tributaries north and west of Stoke-upon-Trent and by the Rudyard Gorge, north of Leek; and (4) by the Market Drayton Gap into the Severn and the Bristol Channel.

February 15th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President in the Chair.

In his Anniversary Address, dealing with the Geological History of the Atlantic Ocean, the President remarked that the Atlantic is the best test case for the theory of the permanence of the ocean basins. According to one view, the Atlantic trough is a primæval geographic feature and dates back to the pre-Palæozoic. According to an alternative view, it has been repeatedly so broken up by lands trending east to west across it that there was no sea entitled to the name of the Atlantic.

The Icelandic Ridge, the northernmost of these cross lands, is generally accepted, and it was probably finally severed between the Upper Palæolithic and the Neolithic. This land is shown by

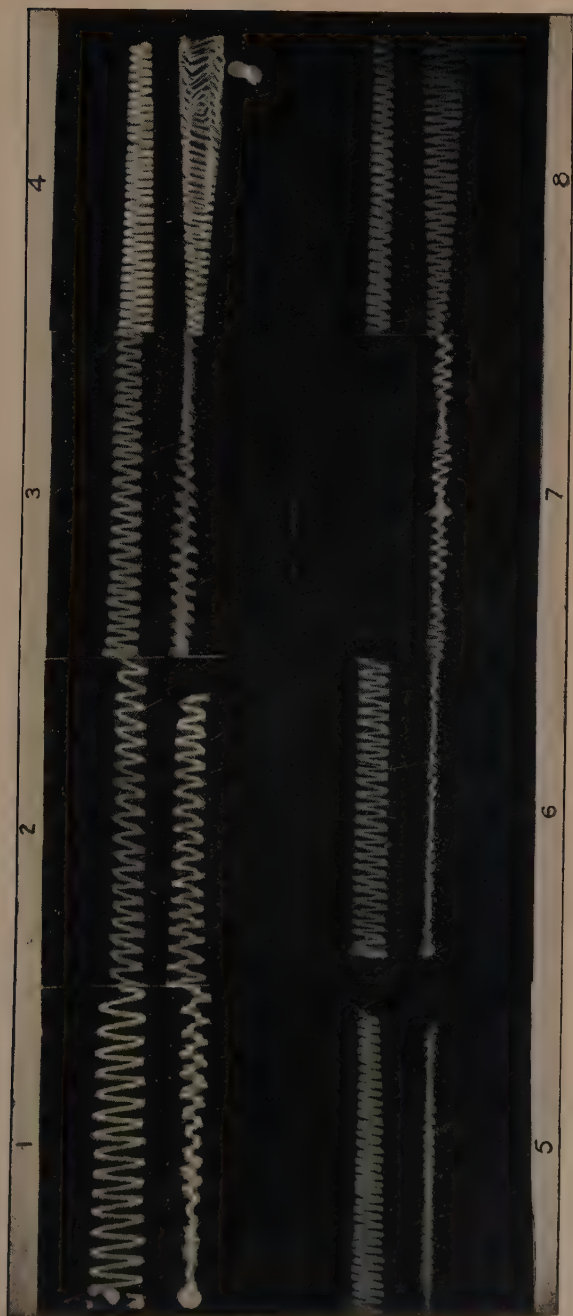
varied evidence from different geological periods to have extended as far south as a line from Newfoundland to Ireland, or to the Azores. It formed the northern shore of the Tethys. The main issue regarding the Atlantic relates to the southern side of the Tethys and the Brazilio-Ethiopian land. That the South Atlantic was occupied by land in the Palæozoic Era is indicated by the absence of marine rocks from most of both coasts. From Upper Carboniferous to Lower Jurassic times Brazil and Africa were parts of Gondwanaland, and a southern fauna and flora ranged through both. The invasion of this land by the sea began in the Middle Cretaceous Period, with gulfs from the Mediterranean which reached Brazil and Angola: they were closed to the south, as the marine fauna of Cape Colony is distinct, and ranged westwards through Chile, and as the freshwater fauna was continuous between Africa and South America. This continuity is shown by the river fishes, porcupines, lizards, snakes, and many invertebrates, of groups that were in existence in the Lower Kainozoic Era. The evidence shows that the connexion lasted till the end of the Oligocene; but it cannot have lasted much later, as the more specialized mammals and birds, for instance, the humming-birds, did not use it as a land bridge. The existence of this land-connexion in Oligocene times is shown by the occurrence of the same shallow-water marine animals in the West Indies and in the Mediterranean. Some of them might have crossed by a chain of islands, but that the land was continuous is shown by the marine mollusca of the West Indies and the Mediterranean being distinct from those in the south. The first commingling in South America was in the Upper Miocene (Entrerios Beds) according to H. von Ihering. A slight temporary land-connexion was established in the Upper Miocene, as shown by the migration of *Hipparion gracile* to Europe and of African antelopes to the United States.

This land-connexion was severed too early to have served as Atlantis, though the Canaries may have been joined to the mainland up to the Pleistocene. There is no geological evidence of any land-connexion of Africa and South America in the time of Man.

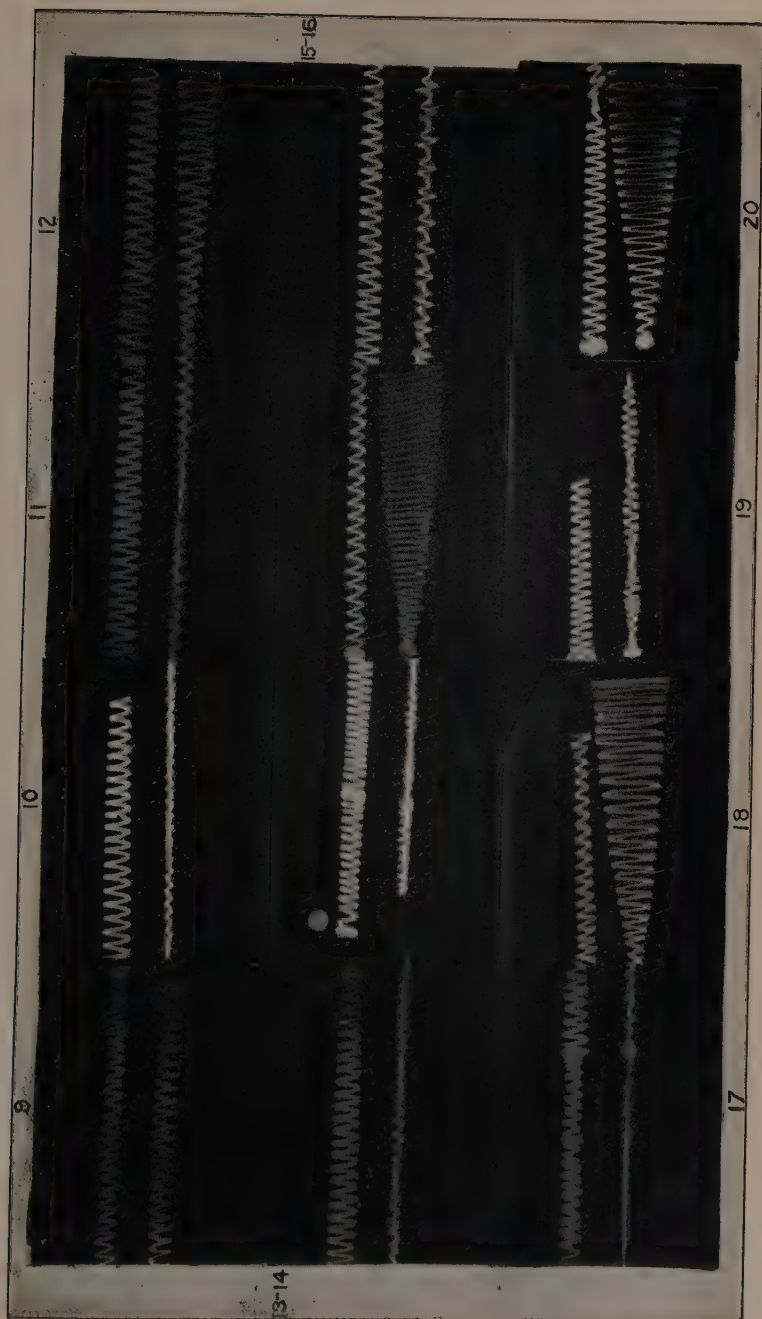
The Atlantic is a relatively young geographical feature and due, as held by Suess, to the growth of two gulfs, which projected northwards and southwards from the Tethys. These gulfs were formed by subsidences which began in the Middle Cretaceous and have continued to the Pleistocene, and they finally united the Arctic, the North Atlantic (Poseidon), and the Nereus of the South Atlantic. The Atlantic trough is the greatest of meridional geographical features, and is due to the collapse of a belt of the crust along faults and tensional fractures connected with the pressure of South America westward against the Andes.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

FIGS. 1-8.



FIGS. 9-20.



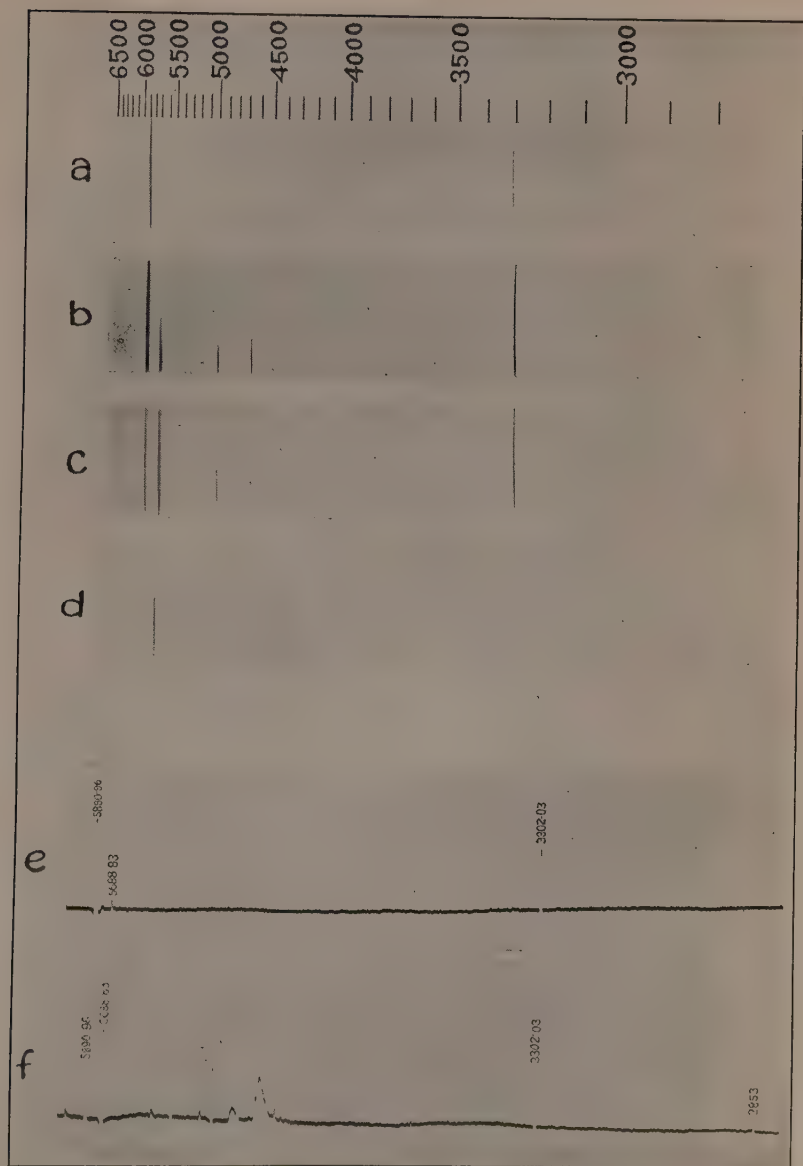




FIG. 1.

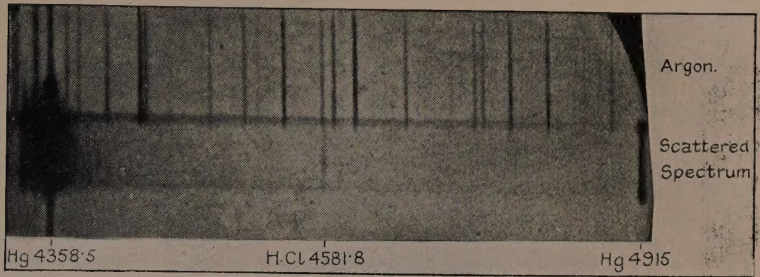


FIG. 2.

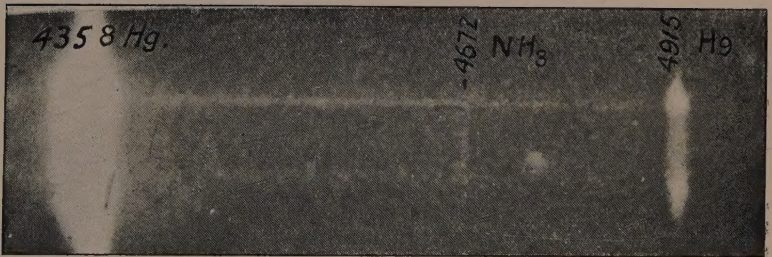


FIG. 3.



